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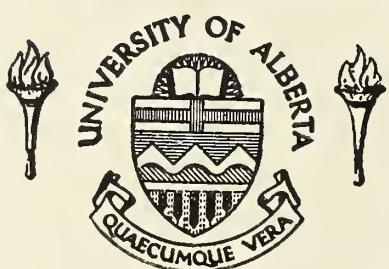
THE UNIVERSITY OF ALBERTA

A THEORETICAL AND EXPERIMENTAL STUDY OF GERMANIUM

ISOTOPE FRACTIONATION

by

Hugh Maitland Brown

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ABSTRACT

In the introduction, several of the more interesting
isotopic composition studies of various elements are con-
sidered in order to indicate a few of the processes which
might alter isotopic abundances in nature.

A theoretical study is then made on isotopic compounds
of germanium. Isotopic vibrational frequencies are calculated
for various Ge^{70} and Ge^{76} containing compounds. From these,
the ratios of the corresponding isotopic vibrational partition
functions are computed. These ratios are then used to
calculate the equilibrium constants for various Ge^{70} - Ge^{76}
exchange reactions at different temperatures. In such
equilibria, variations in the Ge^{70}/Ge^{76} ratio of up to 3.5%
are predicted provided that such exchanges can be effected
experimentally.

Calculations of the minimum and maximum kinetic isotope
effects to be expected in the breaking of various diatomic
bonds also predict isotope effects of the same order.

An experimental study of the reductions

$$Ge^{70}O_2 \xrightarrow{k_1} Ge^{70}O$$
$$Ge^{76}O_2 \xrightarrow{k_2} Ge^{76}O$$
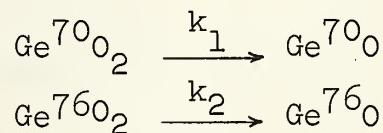
showed the ratio of the rate constants k_1/k_2 to be 1.012 at
$100^{\circ}C$. This result is in agreement with a simplified theore-
tical model of the reaction.

ACKNOWLEDGEMENTS

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INTRODUCTION

A. The History of Isotopes

The first direct evidence for the existence of isotopes
came from studies of the radioactive elements and their trans-
formation products during the first decade of this century.
Workers investigating these decay products found pairs of
atomic species which appeared to be inseparable and identical
in their chemical properties. Boltwood (15), for example,
discovered the radioelement "ionium" in 1906 and found it to
be chemically similar to thorium. Ionium (now Th^{230}) could
be distinguished from common thorium, however, by its different
radioactive behavior. Soddy (70) suggested that this occurrence
of two or more "elements" of identical chemical properties,
but different atomic weights and radioactive properties, was
probably a general phenomenon. It was clear to him that such
"elements" were in effect different atomic forms of the same
element and in 1910 he proposed that they be called "isotopes"
(from the Greek 'isos' meaning 'equal' and 'topos' meaning
'place') to signify that they occupied the same place in the
periodic table.

Sir J. J. Thomson (76) was the first to show that isotopes
of stable elements existed. In 1912, he detected two of the

natural isotopes of neon by the action of electric and magnetic fields on beams of ionized neon atoms. This work was soon followed by the extensive investigations of Aston (5) and Dempster (21) who identified and measured the abundances of the natural isotopes of many elements using their mass spectrographs. The early mass spectrographic studies did not detect the heavy isotopes of carbon, hydrogen, nitrogen, and oxygen (possibly because of their low abundances) and these were first discovered by molecular spectroscopists in the period from 1928 to 1932.

It was found from radioactive disintegration studies that the radioactive series of U^{238} and Th^{232} terminated in Pb^{206} and Pb^{208} respectively. Consequently Richards (66) noted that lead associated with thorium ores had a higher atomic weight than lead associated with uranium ores. Thus, it was known quite early in the history of isotopes that isotopic abundances of elements in deposits could be altered by radioactive transformations. Moreover, if the amount of radioactive product present relative to the amount of undecayed parent is known, the age of the parent mineral can be determined. The age of thorium and uranium deposits, therefore, can be found by isotopic analysis of the lead present. Similarly potassium minerals can be dated by isotopic analyses of the argon present due to the radioactive decay of K^{40} to A^{40}.

Other dating methods include the use of the Rb^{87} to Sr^{87} decay and C^{14} determinations.

It is unfortunate that, in the two decades following the discovery of isotopes, a great deal of data was accumulated to suggest that isotopes of an element were identical chemically and were of constant abundance in nature except where radio-activity was involved. Most of these observations, however, were carried out with heavy atoms. Here the differences sought were too small to be detected by the instruments of that time.

Equilibrium Isotope Effects

A change in the concepts of the chemical behavior of isotopes followed the discovery of deuterium in 1932 by Urey, Brickwedde, and Murphy (81). Since deuterium weighs twice as much as protium it seemed quite illogical that the two should have identical chemical properties. At this time evidence that deuterium and protium behave differently in nature was brought forward by Emeleus et al (25) who found variations of up to eight parts per million in the densities of pure water samples from various geographical locations. This was attributed to variations in the hydrogen isotope abundances.

Urey and Rittenburg (84) next calculated the equilibrium constants for the reaction

$$H_2(g) + D_2(g) \rightleftharpoons 2\ HD(g)$$
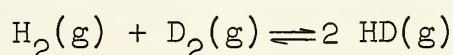
at different temperatures using the methods of statistical mechanics. The equilibrium constants differed from unity indicating that the hydrogen isotopes were, in fact, different chemically. Rittenburg, Bleakney, and Urey (67) found that experimentally determined equilibrium constants for this reaction were close to the theoretical ones.

The theory of equilibrium isotope effects was further developed by Urey and Grieff (83) who also calculated the equilibrium constants for some isotopic reactions of the elements, lithium, boron, carbon, nitrogen, chlorine, and bromine. Experimental confirmations for some of their theoretical predictions were soon obtained. For example, the theory predicted that CO_2 in equilibrium with H_2O would be enriched by 4.4% in O^{18} relative to that of the water at $0^{o}C$. Weber, Wahl, and Urey (88) experimentally found this enrichment to be 4.6%. Many other isotope exchange reactions involving the isotopes of light elements have been studied in recent years and the agreement between theory and experiment has been excellent. A summary of many of these reactions has been made by Urey (79). These researches established the existence of comparatively large differences in the properties of protium and deuterium compounds, and of smaller but significant differences in the chemical properties of isotopic compounds of the elements of low atomic weight.

Kinetic Isotope Effects

Soon after the discovery of deuterium it was found that isotopic molecules react at different rates and, therefore, that kinetic isotope effects exist. This was demonstrated by Urey and Washburn in 1932 (86) with the discovery that partially electrolyzed water was enriched in deuterium since protium was evolved more readily than deuterium at the cathode. Bach, Bonhoeffer, and Fajans (6) showed in 1934 that H_2 reacted with bromine more than three times faster than D_2. In the same year Farkas and Farkas (34) reported similar results with the photochemical reactions of hydrogen and deuterium with chlorine. The extensive work done since this time on the relative reaction rates of hydrogen-and deuterium-containing compounds has been reviewed by Urey and Teal (85) and by Eidinoff (24).

It was not until 1949 that kinetic isotope effects were reported for elements other than hydrogen. In that year carbon isotope effects in the decomposition of oxalic acid and the decarboxylation of malonic acid were found by Lindsay, McElcheran, and Thode (51) and by Bigeleisen and Friedmann (11). These results, which were further studied by Lindsay, Bourns, and Thode (50), were in excellent agreement with theory. Carbon isotope fractionations in a large number of organic reactions have since been studied and considerable literature on these exists.

Reviews on kinetic isotope effects in general have been made by Ropp (68), by Thode (72) and by Craig and Boato (20).

B. Isotope Abundance Variations in Nature

Due to differences in their chemical properties, the isotopes of the light elements fractionate considerably in geological and biological processes. Since the principle of isotope fractionation is now fairly well understood, the isotope abundances that occur in natural substances are indicative of the substances' past chemical and physical history. The study of natural variations in isotope abundances has been carried on extensively. Some of the more interesting examples of isotope fractionations in nature and the mechanisms causing them will be given here.

In 1934 Emeléus et al (25) discovered variations in the density of water samples. The previous year the study of the deuterium content of water was initiated mass spectrometrically by Bleakney and Gould (14). This study was then taken up by a number of workers including Friedmann (36), who showed water samples to have a variation in the H/D ratio of up to 16%. Ocean waters near the equator were found to be enriched in deuterium. It was also observed that there was a gradual depletion of the deuterium content in rainfall samples progressing from the Pacific Coast of North America inland over the Rocky Mountains. Both of these observations were attributed

by Friedmann to the different vapour pressures of H_2O and HDO.
The preferential evaporation of H_2O over HDO was responsible
for the enriched deuterium content of equatorial ocean waters,
while in the rainfall study, HDO condensed faster enriching
the coastal rainfall in deuterium. The remaining vapour,
depleted in HDO, moved further inland before condensation
thus accounting for the gradual decrease in deuterium content
of the rainfall as noted. Fractionations such as this, which
are caused by differences in vapour pressure, are termed
"Rayleigh" fractionations.

Further, a study of fumaroles in Yellowstone Park showed
the deuterium content to be depleted by as much as 45%.
Friedmann suggested that the equilibrium exchange reaction

$$H_2 + HDO \rightleftharpoons HD + H_2O$$
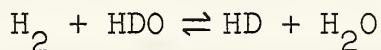
might be the mechanism involved. If this were the case,
theoretical considerations show that the temperature of the
fumaroles would have to be above $400^{\circ}C$.

Oxygen was the next element shown to vary in its natural
isotopic composition. Here again very extensive studies have
been made. Of particular interest is a paleo-temperature
scale suggested by Urey (79) in 1947. If the fractionation
of a known isotopic exchange reaction is measured, it should
be possible to determine the temperature at which the fractiona-
tion occurred, provided that the temperature dependence of the

equilibrium constant of the reaction is large enough. With this in mind Urey (80), Urey et al (82), McCrea (58), and Epstein et al (27) studied the isotopic equilibrium reaction

$$\frac{1}{3} Co_3^{16=} {}_{calcite} + H_2O^{18}{}_{(1)} \rightleftharpoons \frac{1}{3} CO_3^{18=} + H_2O^{16}{}_{(1)}$$
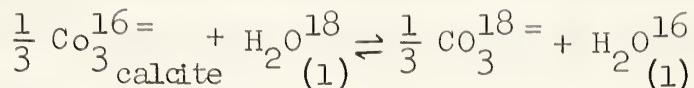
in detail. Clayton (19) found K to be 1.03187 at 25°C with a temperature dependence given by

$$\ln K = 2725 \ T^{-2}$$

Epstein (26) next studied a fossil of a Jurassic belemnite, a marine animal of the mesozoic era (1.2 x 10^8 years ago). According to the equilibrium above, carbonate shells would be enriched in O^{18} over the surrounding water. Carbon dioxide was derived from layers of carbonate in the animal's shell and the O^{18}/O^{16} ratio determined for each layer. A general enrichment in the O^{18} content was found which varied with the successive carbonate layers. These variations were attributed to seasonal changes in the temperature of the water in which the animal lived and, on the basis of the above equation, amounted to temperature fluctuations between 18°C and 24°C. While there is some controversy as to the constancy of the O^{18} content of the oceans through geological time, nevertheless, the experiment was valuable in showing that original carbonate layers are retained through history and that a study of this nature is feasible.

Hoering (47) was the first to report on a series of studies of the isotopes of nitrogen. While the N^{14}/N^{15} ratio was found to be the same for the atmosphere and rocks, it was observed that nitrogen contaminants in natural gas were enriched in N^{14} over the nitrogen found in the associated crude oil. Hoering suggested that migration of the oil and gas through porous deposits was responsible. Migration by molecular flow in which the mean free path of the gas is greater than the pore dimensions results in flow rates of the isotopic molecules which are inversely proportional to the square root of the masses. To give credence to his postulate, Hoering set up laboratory diffusion experiments and was able to produce to some degree the fractionation found in nature.

The study of sulphur isotope abundances has revealed another interesting example of natural variations. Thode, Macnamara, and Collins (74) first showed that the S^{32}/S^{34} ratio varied by as much as 5% in terrestrial sulphur samples. Subsequent investigations extended the observed variations to 8%. Macnamara and Thode (54) also found that samples of sulphur from meteorites had a remarkably constant S^{32}/S^{34} ratio which was close to the average S^{32}/S^{34} ratio for terrestrial samples. They postulated, therefore, that the meteoric S^{32}/S^{34} ratio represented the primordial abundance of terrestrial sulphur before any fractionation processes had occurred.

Tudge and Thode (78) noted that the equilibrium constant for the exchange reaction

$$S^{32}O_4^= + H_2S^{34} \rightleftharpoons S^{34}O_4^= + H_2S^{32}$$
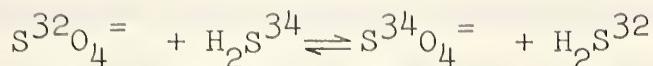
was close to the total variation observed in nature and suggested that this was a possible fractionation reaction. Since the exchange does not occur directly under normal conditions, it was further suggested that the following biological sulphur cycle might provide the mechanism.
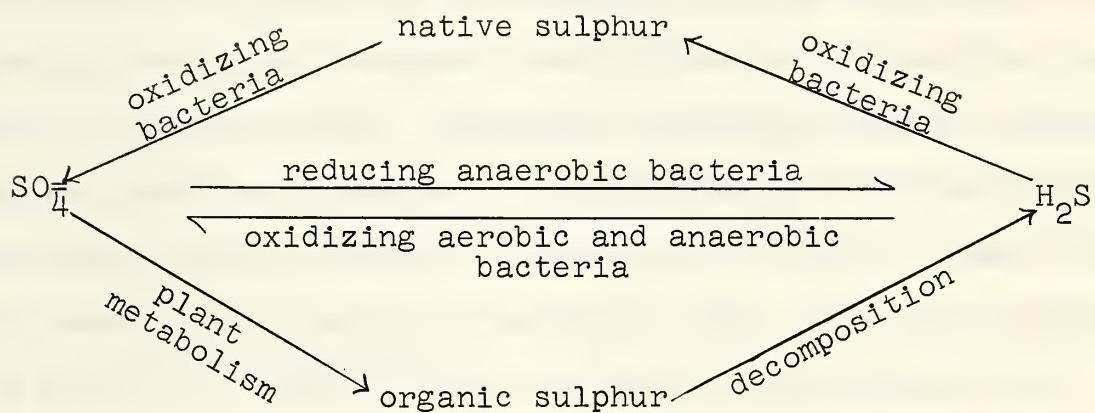
Direct evidence for the fractionation of sulphur in this cycle was obtained from the Cyrenaican Lakes of Africa which were known to abound with anaerobic reducing and photosynthetic hydrogen sulphide oxidizing bacteria. Macnamara and Thode (55) found that the S^{34} content of the elemental sulphur produced by these bacteria was 3.2% less than that of the soluble

sulphate from the same lakes. Further evidence that this cycle is responsible for the fractionation of sulphur isotopes by the reduction of the sulphate is found in the salt domes of Louisiana and Texas. Thode, Wanless, and Wallauch (75) found that the elemental sulphur in these domes was depleted by about 4% and the sulphide by about 5% in S^{34} relative to the associated gypsum. It is possible that the reduction of the sulphate was accomplished by organic matter (oil fields near the salt domes) at high temperatures but this process is incapable of producing the observed isotope fractionation. Bacterial reduction, however, can produce an isotope fractionation of the order noted. Moreover, anaerobic sulphate reducing bacteria have been isolated in these deposits by Miller (60). The organic matter present in the form of crude oil near the salt domes is necessary for bacterial life. Bacteria convert this matter to carbon dioxide and water which changes the calcium sulphate deposits to porous calcite limestone with elemental sulphur embedded in it. This is precisely the type of deposit present in the salt domes today.

Laboratory experiments with sulphate reducing bacteria were first carried out by Thode, Kleerekoper, and McElcheran (73). They were able to show that the bacteria Desulphovibrio desulphuricans while reducing sulphate produced H_2S which was

1% richer in S^{32} than the nutrient. In subsequent studies Harrison and Thode (40) found that this fractionation varied with reaction conditions and that the maximum enrichment was 2.5% at $25^{o}C$.

Other parts of the sulphur cycle have been studied, but as yet only the reduction step has been found to cause an alteration of the S^{32}/S^{34} ratio. In addition, other equilibria have been proposed for specific deposits but, to date, no mechanism has been found to produce directly the 8% variation noted in nature.

In summary, it is seen that Rayleigh fractionation, equilibrium exchange reactions, diffusion, and bacterial reduction are possible mechanisms for altering the isotopic abundances of elements in nature.

C. The Group IV A Elements

General Chemistry

The elements of group IV A (carbon, silicon, germanium, tin, and lead) have atoms with four valence electrons placing them at a half-way point in the periodic table between the electronegative halogens and the electropositive alkali metals. As the atomic number increases in the group there is an increasing tendency for the elements to react with non-metals such as chlorine. Carbon and silicon are mainly non-metallic

in their physical properties while germanium, tin, and lead
are increasingly metallic. Because a large amount of energy
is required to remove all the valence electrons, these ele-
ments do not form simple quadruply charged positive ions; they
show little desire to form simple positive ions of any type.
There is also little tendency to take up four electrons to
form ions of the type M^{4-}. Rather, the majority of the bonds
are covalent and, with the exception of tin and lead, usually
quadricovalent. In these quadricovalent compounds the
oxidation state varies from -4 to +4. The change in oxidation
state of an element during a chemical reaction is one of the
factors which determines the extent to which isotope abundances
may be altered in laboratory or natural processes.

Isotope Abundance Studies

The isotopic abundances of some of the elements of group
IV A have been investigated. Some indication of the isotopic
fractionation to be expected with germanium may be gained
from the results of these studies. In addition to the change
in oxidation state, the chemical and physical behavior and the
percentage mass difference between the isotopes considered
also determine the possible isotope fractionation of an element.
Carbon and silicon are now discussed with reference to these
points.

With the exception of hydrogen, carbon has been more

extensively studied with respect to isotope effects than any
other element. The effect in many organic reactions has been
measured but the results sometimes differ from those predicted
theoretically. This is due, in part, to the general complexity
of the chemical behavior of carbon.

Between C^{13} and C^{12} there is a mass difference of 1 in
12 or a percentage mass difference of 8.3%. Further, carbon
is found in many physical forms and oxidation states in nature.
As a consequence, it is expected that carbon will undergo
significant isotope fractionation while participating in its
many biochemical and geochemical reactions. A variation of
5% in the C^{12}/C^{13} ratio was first reported in 1939 by Nier
and Gulbransen (61). These results were later confirmed and
a great deal of additional information supplied by numerous
workers including Craig (20). It was generally found that
limestones were enriched and plants depleted in C^{13} with
respect to the atmospheric C^{12}/C^{13} ratio. It is suggested
that this carbonate-atmospheric CO_2 difference is due to the
simple exchange reaction

$$C^{13}O_2 + C^{12}O_3^{=} \rightleftharpoons C^{12}O_2 + C^{13}O_3^{=}$$
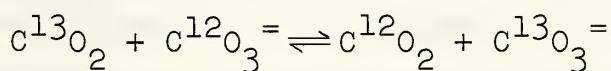
for which Urey (79) calculated the equilibrium constant to be
1.012 at $25^\circ C$. Sea plants concentrate C^{12} to a lesser degree
than do land plants and it has been proposed that this results

from differences in the cellular structure of the plants.
Biological fractionation has also been observed in the labora-
tory by Franck and Urey (35). They found that the assimilation
of C^{12} by algae from a nutrient broth was 2.8% faster than
assimilation of C^{13}.

In contrast to carbon, very little has been done to date
in studies of silicon. Two of the silicon isotopes Si^{28} and
Si^{30} have a mass difference of 2 in 28 or a percentage mass
difference of 7%. In addition, silicon is usually found in
the +4 oxidation state as silicates in nature. Because of
this uniformity, one does not expect the isotopes of silicon
to be fractionated to the same extent as those of carbon.
Earlier studies were made by Marsden (56), Reynolds and Verhoogen
(65), and Allenby (1). All workers, except Allenby, found
variations in the Si^{28}/Si^{30} ratio of up to 0.3%, whereas
Allenby found variations of up to 1.3%. In general, the Si^{30}
content was found to decrease from high temperature minerals
such as olivine to low temperature minerals such as pegmatite
quartz. Organic silica from sea water (e.g. chert and marine
diatomite) had a greater Si^{30} content than olivine. Grant (39)
has discussed theoretically various physical and chemical
processes which might lead to fractionation of the silicon
isotopes and concludes that diffusion processes are not likely
involved. Results of calculations are given for equilibria of

minerals in a common magma and isotopic fractionation by precipitation from solutions is discussed. Tilles (77) has more recently found the overall variation of the Si^{28}/Si^{30} ratio to be about 0.5%. Biotite, quartz, and feldspar coexisting in the same igneous rock differed by 0.3% in their isotope ratio with the feldspar enriched in Si^{30}. The enriched feldspars were believed to have resulted from Rayleigh fractionation during crystallization from a vapour phase.

Germanium

The third element of group IV A, germanium, was first isolated in 1886 by C. Winkler who recognized from its properties that it fitted the place of eka-silicon in Mendeléeff's periodic table. It was given the name germanium from the Latin Germania, the country of its discovery.

The isotopes of germanium were first investigated by Aston (2) in 1923. Using a product obtained by the action of HF on GeO_2 he identified isotopes of mass number 70, 72, and 74 and roughly estimated their proportions. Aston (3) continued his investigations in 1928 with an improved photographic plate in his mass spectrograph. He found eight isotopes of mass numbers 70, 71, 72, 73, 74, 75, 76, and 77 using $Ge(C_2H_5)_4$ and GeF_4 as ion sources. The results of further work with $Ge(CH_3)_4$ were published in 1931 (4). The following year Shapiro et al (69) reported abundances for mass

numbers 70, 72, 74, and 76 comparable to those found by Aston.
Their results were based on investigations of the absorption
band spectra of GeS. They were unable to detect mass numbers
75 and 77 and considered that the bands due to Ge^{71} and Ge^{73},
if present, would be masked by the strong bands of Ge^{70}, Ge^{72},
and Ge^{74}. Bainbridge (7,8) examined germanium in 1933 using
the bromide and iodide and concluded that the isotopes Ge^{71},
Ge^{75}, and Ge^{77} as reported by Aston were "mainly if not entirely"
hydrides of Ge^{70}, Ge^{74}, and Ge^{76}. The possibility of hydride
formation had been recognized by Aston as early as 1928.
After publication of Bainbridge's results, Aston applied a
correction to his work of 1931 and agreed that the isotopes
reported at masses 71, 75, and 77 were due to hydrides and
that the existence of these isotopes was doubtful. Until
very recently these corrected values have been the accepted
ones for the germanium isotopes.

More recent studies of germanium began in 1947 when Inghram,
Hayden, and Hess (48) measured the ion currents of Ge^{+} and
Ge^{++}. Hibbs, Redmond, Gwinn, and Harmon (45) measured the
spectra of GeI_4 and GeF_4 in 1949. They used a Nier-type mass
spectrometer and observed the ion currents of GeF_3^{+} and GeI^{+}
with an electrometer tube.

A very careful study of the isotopes of germanium was
made in 1951 by Graham, Macnamara, Crocker, and MacFarlane (38).

Their mass spectrometric study was based on measurements of the ion currents of GeF_3^+ and $GeCl^+$ using a 180° direction focussing instrument. In the course of their work six different samples of germanium-bearing material from widely varying geographical and geological origins were investigated. These included samples of germanite from Tsumeb, South-West Africa, flue dusts of coals from Durham, England, and zinc ores from the Tri-State area of the U.S.A. Within the precision of their measurements, Graham et al found all but one of the samples to have the same isotope abundances. According to statistical tests applied to the data, the one sample differed significantly. This was the first time that evidence of variations in the natural isotope abundances of germanium had been found. The variation amounted to 0.7% in the Ge^{76}/Ge^{70} ratio.

The latest isotopic determination of germanium found in the literature was done by Reynolds (64) in 1953 who was unaware of the work of Graham et al until just before his results were published. He used a nine-inch radius 60° single focussing mass spectrometer to measure the ion currents of GeF_3^+. Table I summarizes the results of Reynolds and those of the other investigators mentioned above.

TABLE I

Absolute Abundances of the Isotopes of Germanium

REFERENCE AND YEAR	Aston 1933 (4)	Inghram et al 1947 (48)	Hibbs et al 1949 (45)		Graham, Macnamara, Crocker, and MacFarlane 1951 (38)				Reynolds 1953 (64)
INSTRUMENT	mass spectrograph, photometric detection	60° mass spectrometer, electronic detection	Nier-type mass spectrometer, electronic detection magnetic scanning		180-degree direction focussing spectrometer, magnetic scanning, electronic detection				9 in radius 60° single focussing spectrometer
SOURCE OF IONS	$Ge(CH_3)_4$		GeF_4	GeI_4	GeF_4		$GeCl_4$		GeF_4
		Ge^+, Ge^{++}	GeF_3^+	GeI^+	GeF_3^+		$GeCl^+$		GeF_3^+
MASS NUMBER					A	B	A	B	
70	21.2	20.55	20.60	20.65	20.45	20.38	20.27	20.23	20.52
72	27.3	27.37*	27.38	27.43	27.41	27.37	27.37	27.30	27.43
73	7.9	7.67	7.83	7.86	7.77	7.78	7.70	7.70	7.76
74	37.1	36.74	36.40	36.34	36.58	36.65	36.80	36.87	36.54
76	6.5	7.67	7.78	7.72	7.79	7.82	7.86	7.90	7.76

PERCENTAGE ABUNDANCE

*The value given for Ge^{73} in (48) is a misprint (38).

A. Fractionated sample; B. All other samples.

THEORY

At the present time the theory of isotope fractionation is well understood and with a knowledge of the fundamental vibrational frequencies of a particular molecule, it is possible to calculate the extent to which a chemical process might fractionate the isotopes of an element in this molecule. The theory, which is briefly summarized below, can be found in a number of references (13, 59). Urey (79) gives a good development of the equilibrium isotope effect while an excellent review of the literature concerning the kinetic isotope effect is given by Bigeleisen and Wolfsberg (13).

A. The Theory of Equilibrium Isotope Effects

Urey and Rittenberg (84) were the first to show by theoretical calculations that marked differences in the equilibrium constants of isotopic exchange reactions should exist. The theory was stated more explicitly in a similar paper by Urey and Grieff (83). Later simplification by Urey (79) and by Bigeleisen and Mayer (12) has made it possible to calculate the equilibrium constants of isotopic reactions solely with a knowledge of the vibrational frequencies of the isotopic molecules.

An isotopic exchange reaction may be written

$$aA_1 + bB_2 \rightleftharpoons aA_2 + bB_1 \tag{1}$$

where the subscripts 1 and 2 refer to the light and heavy isotopes respectively and A and B are molecules having the element under consideration as a common constituent.

According to a well known theorem of thermodynamics (57), the equilibrium constant of this exchange is given in terms of the standard free energy change ΔF° by

$$-RT \ln K = \Delta F^{O} = aF_{A_2} + bF_{B_1} - aF_{A_1} - bF_{B_2} \tag{2}$$

The free energy, in turn, can be expressed in terms of the total partition function using the relation (57) from statistical mechanics

$$F = E^{O} + RT \ln N - RT \ln Q \tag{3}$$

where N is Avogadro's number, E^{O} is the total standard zero-point energy, and Q is the total partition function given by

$$Q = \sum_n g_n \, e^{-\epsilon_n/kT} \tag{4}$$

g_n is the statistical weight factor. Here the summation extends over all quantum states of energy ϵ_n, a d-fold degenerate level counting as d states. To a first approximation the total partition function may be written as the product of translational,

rotational, and vibrational partition functions. The trans-
lational partition function is classical at all temperatures
and is given by

$$Q_{TR} = V \left[\frac{2 \pi m\, kT}{h^2} \right]^{3/2}$$

while the rotational partition function is classical at room
temperatures in all cases except for hydrogen. If the spin
contribution, electronic energy levels, anharmonicity and
non-rigidity are neglected and if all internal energies are
referred to the lowest state (zero point energy) of the mole-
cule, then the total partition function for linear molecules
is given by

$$Q = V \left[\frac{2 \pi m\, kT}{h^2} \right]^{3/2} \cdot \frac{\frac{kT}{\sigma hc\, B_o}}{(1 - e^{-\omega_1 hc/kT})^{d_1} (1 - e^{-\omega_2 hc/kT})^{d_2} \cdots} \qquad (5)$$

and for non-linear molecules by

$$Q = V \left[\frac{2 \pi m\, kT}{h^2} \right]^{3/2} \cdot \frac{\frac{1}{\sigma} \sqrt{\frac{\pi}{ABC} \left[\frac{kT}{hc} \right]^3}}{(1 - e^{-\omega_1 hc/kT})^{d_1} (1 - e^{-\omega_2 hc/kT})^{d_2} \cdots} \qquad (6)$$

The bracketed second term consists of the rotational and vibrational terms and is called the internal partition function or 'summation of state.' In equations (5) and (6)

d_i is the degree of degeneracy of frequency ω_i

B_o is the rotational constant of the linear molecule

A, B, and C are the principal moments of inertia of the polyatomic molecule, and

σ is the symmetry number introduced to take account of the identity of nuclei.

It is found that for all molecules, except hydrogen, the contributions to Q which have been ignored above are negligible and that equations (5) and (6) are suitable for most calculations of thermodynamic quantities, except at low temperatures where the rotational partition function is not classical.

In equation (3) if one molecule in unit volume is considered instead of one mole, the free energy becomes

$$F = E^O - RT \ln Q \qquad (7)$$

Solving for K in equations (2) and (7) then yields

$$K = \left\{ \left[\frac{QA_2}{QA_1} \right]^a \Big/ \left[\frac{QB_2}{QB_1} \right]^b \right\} \exp. \left[\frac{aE_{A_2}^O + bE_{B_1}^O - aE_{A_1}^O - bE_{B_2}^O}{RT} \right] \qquad (8)$$

It has been found experimentally that the potential energy curves

of isotopic molecules are identical to a high degree. If they
are assumed identical, then equation (8) can be further
simplified by referring all energies to the minimum of the
potential energy curve rather than to the zero point energy
levels. This shift of energy reference removes the exponential
dependence of equation (8) and the equilibrium constant becomes

$$K = \left[\frac{QA_2}{QA_1}\right]^a \bigg/ \left[\frac{QB_2}{QB_1}\right]^b \qquad (9)$$

Equation (9) is simply the ratios of the partition functions
for the two isotopically substituted molecules. For linear
molecules equations (5) and (6) are used in turn to form the
partition function ratio

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \frac{I_2}{I_1} \left[\frac{M_2}{M_1}\right]^{3/2} \frac{e^{-u_2/2}(1 - e^{-u_1})}{e^{-u_1/2}(1 - e^{-u_2})} \qquad (10)$$

while for polyatomic molecules the ratio is

$$\frac{Q_2}{Q_1} = \frac{\sigma_1}{\sigma_2} \left[\frac{A_2 B_2 C_2}{A_1 B_1 C_1}\right]^{1/2} \left[\frac{M_2}{M_1}\right]^{3/2} \pi_i \frac{e^{-u_{2i}/2}(1 - e^{-u_{1i}})}{e^{-u_{1i}/2}(1 - e^{-u_{2i}})} \qquad (11)$$

In these equations

M_1, M_2 are the molecular weights of the molecules,

I_1, I_2 are the moments of inertia of the linear molecules,

$u_1 = \frac{hc}{kT} \omega_1$ and ω_1 is the vibrational frequency in cms^{-1}.
The product π_i extends over all "i" fundamental frequencies of
the polyatomic molecule.

Urey simplified the above expressions and defined new
partition functions which were, in fact, the equilibrium
constants for exchange reactions between the compound considered
and the separated atoms. Both sides of equations (10) and
(11) are multiplied by $\left[\frac{m_1}{m_2}\right]^{3/2n}$ where m_1 and m_2 are the atomic
weights of the isotopic atoms being considered and n is the
number of isotopic atoms exchanged. Further, the right sides
of (10) and (11) are multiplied and divided by $\left(\frac{u_1}{u_2}\right)$ and
$\pi_i\left(\frac{u_{1_i}}{u_{2_i}}\right)$ respectively. According to the theorem of Teller and
Redlich (53)

$$\frac{I_2}{I_1}\left[\frac{M_2}{M_1}\right]^{3/2}\left[\frac{m_1}{m_2}\right]^{3/2n}\left(\frac{u_1}{u_2}\right) = \left[\frac{A_2 B_2 C_2}{A_1 B_1 C_1}\right]^{1/2}\left[\frac{M_2}{M_1}\right]^{3/2}\left(\frac{m_1}{m_2}\right)^{3/2n}\pi_i\left(\frac{u_{1_i}}{u_{2_i}}\right) \quad (12)$$

$$= 1$$

On carrying out the steps above and using (12), equations (10)
and (11) become

$$\frac{Q_2'}{Q_1'} = \frac{\sigma_1}{\sigma_2}\frac{u_2}{u_1} \cdot \frac{e^{-u_2/2}\left(1 - e^{-u_1}\right)}{e^{-u_1/2}\left(1 - e^{-u_2}\right)} \quad (13)$$

and

$$\frac{Q_2'}{Q_1'} = \frac{\sigma_1}{\sigma_2} \; \pi_1 \; \frac{u_{2_i}}{u_{1_i}} \cdot \frac{e^{-u_{2_i}/2} \, (1 - e^{-u_{1_i}})}{e^{-u_{1_i}/2} \, (1 - e^{-u_{2_i}})} \tag{14}$$

The equilibrium constant now is given by

$$K = \left[\frac{Q_{2A}'}{Q_{1A}'}\right]^a \Bigg/ \left[\frac{Q_{2B}'}{Q_{1B}'}\right]^b \tag{15}$$

where $\dfrac{Q_2'}{Q_1'} = \left[\dfrac{M_1}{M_2}\right]^{3/2n} \cdot \dfrac{Q_2}{Q_1}$ is the relation between the new

partition function ratio and the old ratio. K can now be
calculated with only a knowledge of the vibrational frequencies
of the isotopic molecules. These frequencies are obtained
either by direct observation or (as in the case of rarer
isotopes) by calculation from observations on a more abundant
isotope by means of force equations.

For precise calculations of K it is necessary to include
the anharmonic terms in the vibrational energy. A further
correction is also necessary when the rotational partition
functions have not reached classical values as in the case
of hydrogen at room temperature. Urey discusses such correc-
tions and also further simplifies expressions (13) and (14)
by means of a geometric expansion. A more convenient expression,
however, is given by Bigleisen and Mayer (12). They put
$u_{1_i} = u_{2_i} + \Delta u_i$ where u_{1_i} refers to the lighter molecule so

that Δu_1 is always positive. Equation (14) then becomes

$$\frac{Q_2'}{Q_1'} = \frac{\sigma_1}{\sigma_2} \; \pi_1 \left[\frac{u_{2_i}}{u_{2_i} + \Delta u_i} \right] \cdot \left[e^{\Delta u_i/2} \frac{(1 - e^{-u_{2_i} - \Delta u_i})}{(1 - e^{-u_{2_i}})} \right] \quad (16)$$

This equation is the diatomic case if i = 1. For all cases except the isotopes of hydrogen u_i is small so that (16) may be simplified to

$$\frac{Q_2'}{Q_1'} = \frac{\sigma_1}{\sigma_2} \left\{ 1 + \sum_i (\frac{1}{2} - \frac{1}{u_{2_i}} + \frac{1}{e^{u_{2_i}-1}}) \Delta u_i \right\} \quad (17)$$

where in the summation over the "i" fundamental frequencies a d-degenerate frequency must be counted d times. The ratio of symmetry numbers will be unity if the molecule under consideration contains only one atom of the element for which an exchange is considered. The ratio is also unity if the molecule contains more than one such atom but these atoms occupy indistinguishable positions in the molecule and are all exchanged in the reaction. Since Δu_i is positive $\frac{Q_2'}{Q_1'}$

will always be greater than unity. That is, the heavy isotope is more stable in the molecule while the light isotope favors the separated atoms. The function

$$G(u_{2_i}) = \left\{ \frac{1}{2} - \frac{1}{u_{2_i}} + \frac{1}{(e^{u_{2_i}} - 1)} \right\}$$

has been tabulated by Bigeleisen and Mayer (12) giving values
of $G(u_{2_1})$ for u = 0 to u = 25 thus greatly simplifying the
calculation of equilibrium constants.

B. The Theory of the Kinetic Isotope Effect

   The general problem of reaction rates has been developed
from a statistical viewpoint by Eyring (33) and by Evans and
Polanyi (28). Bigeleisen (10) has used their "theory of
absolute rates" and collision theory to develop formulae
which predict the kinetic isotope effect.

   The theory of absolute reaction rates requires the existence
of an "activated complex" between reactant and product. If
the potential energy of a system of atoms in their lowest
electronic quantum states is plotted against the distances
of separation between the nuclei, a potential energy surface
results which determines the motion of the nuclei during a
chemical reaction. The system of atoms moving on this surface
will have kinetic energy quantized for the different degrees
of freedom consistent with its particular position on the
surface. Minima on the potential surface correspond to
compounds; the lower the depth, the more stable the compound.
A reaction corresponds to a system passing from one low region
to another. Thermal reactions will proceed by way of the
lowest energy pass or barrier between the reactant and product
minima because of the Boltzmann factor. The activated state is

the highest energy point on this lowest barrier, that is, a saddle point with positive curvature in all degrees of freedom except the one in the direction of the reaction path. The system at this point is the activated complex.

Consider the reactions of A_1, B, C ... to give product P_1 and A_2, B, C ... to give product P_2 where A_1 is the lighter isotopic molecule and A_2 the heavier.

$$A_1 + B + C + \ldots \xrightarrow{k_1} P_1$$

$$A_2 + B + C + \ldots \xrightarrow{k_2} P_2$$
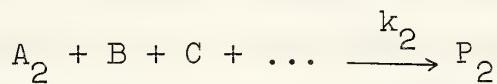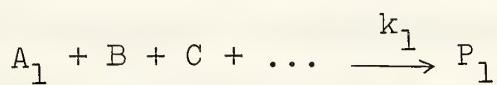
According to the Eyring method the rate constants will be given by

$$k_1 = K_1 \left[\frac{C_1^{\ddagger}}{C_{A_1} C_B C_C \cdots} \right] \left[\frac{kT}{2\pi m_1^*} \right]^{1/2} \cdot \frac{1}{\delta_1} \tag{18}$$

$$k_2 = K_2 \left[\frac{C_2^{\ddagger}}{C_{A_2} C_B C_C \cdots} \right] \left[\frac{kT}{2\pi m_2^*} \right]^{1/2} \cdot \frac{1}{\delta_2} \tag{19}$$

where K_i is the transmission coefficient

$C^{\ddagger}$ is the concentration of the activated complex

m^* is the effective mass of the complex along the coordinate of decomposition and is usually taken to be the reduced mass of the atoms whose bond is directly involved in the reaction.

δ is the length of the top of the potential barrier which the complex traverses.

It has been noted that the potential energy surfaces of isotopic molecules are identical to a high degree. Thus $\delta_1 = \delta_2$ and

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} \cdot \frac{C_1^{\ddagger}}{C_2^{\ddagger}} \cdot \frac{C_{A_2}}{C_{A_1}} \left[\frac{m_2^*}{m_1^*} \right]^{1/2} \qquad (20)$$

From statistical mechanical considerations the ratio of the concentrations of the individual molecules can be replaced by the ratio of their complete partition functions, and

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} \cdot \frac{Q_1^{\ddagger}}{Q_2^{\ddagger}} \cdot \frac{Q_{A_2}}{Q_{A_1}} \left[\frac{m_2^*}{m_1^*} \right]^{1/2} \qquad (21)$$

As in the case of equilibrium isotope effects, the zero of the energy scale for the molecules is chosen as the minimum of the potential energy curve, while for the activated complex the minimum in the saddle of the potential energy surface is chosen for the zero of the energy scale. These are suitable zeros because they simplify the expression for the ratios of the partition functions. The ratio of the complete partition functions of two isotopic molecules, moreover, can be expressed as a simple function of the vibrational energy levels of the two molecules provided the rotational levels have become

classical at the reaction temperature. This was discussed in part A of the theory. Thus equation (21) becomes

$$\frac{k_1}{k_2} = \frac{K_1}{K_2} \; \frac{f}{f^{\neq}} \left[\frac{m_2^*}{m_1^*}\right]^{1/2} \tag{22}$$

where

$$f = \frac{Q'_{A_2}}{Q'_{A_1}} \; \pi_i \left[\frac{M_{i_1}}{M_{i_2}}\right]^{3/2}$$

$$f^{\neq} = \frac{Q'_2{}^{\neq}}{Q'_1{}^{\neq}} \; \pi_i \left[\frac{M_{i_1}}{M_{i_2}}\right]^{3/2}$$

M_i are the masses of the isotopic atoms in the isotopic molecules,

and where

$$\frac{Q'_{A_2}}{Q'_{A_1}} = \frac{\sigma_1}{\sigma_2} \left(1 + \sum_i^{3n-6} G(u_i)\Delta u_i\right)$$

An expression similar to this last one may also be written for the partition functions of the activated complex. That is

$$\frac{Q'_2{}^{\neq}}{Q'_1{}^{\neq}} = \frac{\sigma_1^{\neq}}{\sigma_2^{\neq}} \left(1 + \sum_i^{3n'-6} G(u_i^{\neq})\Delta u_i^{\neq}\right).$$

In the case where Δu_i is small equation (22) is used to give

$$\ln \frac{k_1}{k_2} \cdot \frac{\sigma_2}{\sigma_1} \cdot \frac{\sigma_1^{\neq}}{\sigma_2^{\neq}} = \ln \frac{K_1}{K_2} + \frac{1}{2} \ln \frac{m_2^*}{m_1^*} + \sum_i^{3n-6} G(u_i)\Delta u_i$$

$$- \sum_i^{3n'-6} G(u_i^{\neq})\Delta u_i^{\neq}.$$

On rearranging and neglecting terms in the exponential expansion, one obtains

$$\frac{k_1}{k_2} = \frac{\sigma_1}{\sigma_2} \cdot \frac{\sigma_2^{\ddagger}}{\sigma_1^{\ddagger}} \cdot \frac{K_1}{K_2} \left[\frac{m_2^{*}}{m_1^{*}}\right]^{\frac{1}{2}} \left\{ 1 + \sum_{i}^{3n-6} G(u_i)\Delta u_i - \sum_{i}^{3n'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger} \right\} \tag{23}$$

Hirschfelder and Wigner (46) have studied the absolute value of the transmission coefficient K and its dependence on the properties of the potential energy surface of the activated complex. They conclude that for systems above room temperature which have a distribution in the velocities of the reacting isotopic molecules, the difference in transmission coefficients is small. Thus the ratio of coefficients is near unity.

The derivation above ignores the tunnel effect which Bigeleisen (10) corrects for in a further development. The equation is also difficult to apply since a number of the properties of the activated complex must first be evaluated. However, it is useful in a qualitative description of the kinetic isotope effect.

From equation (23) it can be seen that the light molecule usually has the greater rate constant. This results because the factor $\left[\frac{m_2^{*}}{m_1^{*}}\right]^{\frac{1}{2}}$ is always greater than unity and because the

reacting molecule is usually more tightly bound than the
activated complex. That is

$$\sum_i^{3n-6} G(u_i)\Delta u_i > \sum_i^{3n'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}$$

Only when

$$\sum_i^{3n'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger} > \sum_i^{3n-6} G(u_i)\Delta u_i + \frac{1}{2}\ln\left[\frac{m_2^{\ast}}{m_1^{\ast}}\right]$$

will the rate constant for the heavier molecule be greater,
resulting in an inverse isotope effect.

It should be noted that the ratio $\left[\dfrac{m_2^{\ast}}{m_1^{\ast}}\right]$ is the ratio of
the reduced masses of the activated complex along the reaction
coordinate and is usually taken to be the reduced mass of the
bond directly involved in the reaction. Bigeleisen and Wolfs-
berg (13) suggest, however, that because the molecule is
being torn into two fragments, the reduced mass of the two
fragments should be considered. Wolfsberg (89) discusses the
controversy more explicitly as follows. Consider a molecule
X - A - B - Y in which the A - B bond is broken. If the
A - B bond is strong compared to the X - A, B - Y bonds, then
the latter will shorten as the former lengthens and the
reduced mass term will be closer to $\dfrac{AB}{A + B}$. If, however, the
A - B bond is the weaker, then the reduced mass will be closer

to $\dfrac{M_{XA} \cdot M_{XB}}{M_{XA} + M_{XB}}$ since the mass centres M_{XA} and M_{XB} are being

separated.

Since very little is known about the nature of the activated
complex, the rate constant cannot be evaluated specifically.
Upper and lower limits can be determined for it, however.
These limits are the following.

(a) If the activated complex is like the reactant, then

$$\sum_{i}^{3n-6} G(u_i)\Delta u_i \approx \sum_{i}^{3n'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger}$$

in equation (23) and the ratio of the rate constants
is simply the ratio of the reduced masses; the ratio
takes on its lowest possible value.

(b) If the activated complex is like the product, the
bond has been completely ruptured and

$$\sum_{i}^{3n'-6} G(u_i^{\ddagger})\Delta u_i^{\ddagger} \approx \left\{ \sum_{i}^{3n-6} G(u_i)\Delta u_i \right\}_{product.}$$

In the case of a diatomic molecule

$$\left\{ \sum_{i}^{3n-6} G(u_i)\Delta u_i \right\}_{product} = 0;$$ the ratio of the rate

constants is a maximum. In practice one would expect any
observed effect to be somewhere between these two extremes.

THEORETICAL CALCULATIONS AND RESULTS

In an attempt to determine what isotope fractionation
might be expected in germanium isotope exchange reactions,
the partition function ratios for various molecules contain-
ing Ge^{70} and Ge^{76} have been calculated. Appendix A contains
calculations of vibrational frequencies for some Ge^{70} and
Ge^{76} containing compounds for which molecular data such as
symmetry type and fundamental vibrational frequencies were
available. For the diatomic species, anharmonicity correc-
tions were made. Except where noted the experimentally
observed fundamental frequencies were assumed to apply to
the compounds containing the most abundant isotope Ge^{74}.
The frequencies of the Ge^{70} and Ge^{76} containing molecules
were then calculated by means of 'normal force equations'
from these observed values.

For molecules of the tetrahedral symmetry type several
sets of normal force equations were available corresponding
to several different molecular models. Usually the set of
equations used was one for which force constants had already
been calculated and which described the particular molecule
satisfactorily. Otherwise the force constants for a molecule
were calculated by substituting the known fundamental frequencies

into a set of force equations. Since there were four force equations but only three unknown force constants it was possible to fit the calculated constants to the observed frequencies. These constants along with the isotopic masses were then used to calculate the frequencies for the Ge^{70} and Ge^{76} cases.

Calculations of the ratios of the partition functions of Ge^{70} and Ge^{76} containing molecules at $0^{o}C$, $25^{o}C$, $100^{o}C$, and $250^{o}C$ are found in Appendix B. These were made using the Bigeleisen-Mayer equation (17) and tables of the $G(u_i)$ function along with the calculated isotopic frequencies from Appendix A.

The results of some of these calculations are shown in Table II, along with equilibrium constants for possible isotopic exchange reactions between any two compounds in the table. The values of $\frac{Q'_2}{Q'_1}$ for the four temperatures considered are found in the top row underneath the symbol for the compound. Equilibrium constants, found in the body of the table, are for isotopic exchange reactions between the compounds listed along the top of the table and those listed in the far right-hand column. A constant greater than unity means that the heavier isotope is concentrated in the compound in the left-hand column.

Consider as an example the species GeO at the top of the

TABLE II

Equilibrium Constants for $Ge^{76} \rightleftharpoons Ge^{70}$ Exchange Reactions

Reaction	TEMP °C	$\dfrac{Ge^{76}F_4}{Ge^{70}F_4}$	$\dfrac{Ge^{76}Cl_4}{Ge^{70}Cl_4}$	$\dfrac{Ge^{76}Br_4}{Ge^{70}Br_4}$	$\dfrac{Ge^{76}H_4}{Ge^{70}H_4}$	$\dfrac{Ge^{76}O^{16}}{Ge^{70}O^{16}}$	$\dfrac{Ge^{76}Se^{80}}{Ge^{70}Se^{80}}$	$\dfrac{Ge^{76}S^{32}}{Ge^{70}S^{32}}$	$\dfrac{Ge^{76}Te^{130}}{Ge^{70}Te^{130}}$
Q_2/Q_1	0	1.041	1.023	1.019	1.015	1.012	1.009	1.008	1.006
	25	1.035	1.020	1.016	1.013	1.011	1.007	1.007	1.005
	100	1.024	1.013	1.010	1.009	1.007	1.005	1.005	1.003
	250	1.013	1.007	1.005	1.006	1.004	1.003	1.003	1.002
$\dfrac{Ge^{76}F_4}{Ge^{70}F_4}$	0	1.000	1.018	1.022	1.026	1.029	1.032	1.033	1.035
	25		1.015	1.019	1.022	1.024	1.028	1.028	1.030
	100		1.011	1.014	1.015	1.017	1.019	1.019	1.021
	250		1.006	1.008	1.007	1.009	1.010	1.010	1.011
$\dfrac{Ge^{76}Cl_4}{Ge^{70}Cl_4}$	0		1.000	1.004	1.008	1.011	1.014	1.015	1.017
	25			1.004	1.007	1.009	1.013	1.013	1.015
	100			1.003	1.004	1.006	1.008	1.008	1.010
	250			1.002	1.001	1.003	1.004	1.004	1.005
$\dfrac{Ge^{76}Br_4}{Ge^{70}Br_4}$	0			1.000	1.004	1.007	1.010	1.011	1.013
	25				1.003	1.005	1.009	1.009	1.011
	100				1.001	1.003	1.005	1.005	1.007
	250				0.999	1.001	1.002	1.002	1.003
$\dfrac{Ge^{76}H_4}{Ge^{70}H_4}$	0				1.000	1.003	1.006	1.007	1.009
	25					1.002	1.006	1.006	1.008
	100					1.002	1.004	1.004	1.006
	250					1.002	1.003	1.003	1.004
$\dfrac{Ge^{76}O^{16}}{Ge^{70}O^{16}}$	0					1.000	1.003	1.004	1.006
	25						1.004	1.004	1.006
	100						1.002	1.002	1.004
	250						1.001	1.001	1.002
$\dfrac{Ge^{76}Se^{80}}{Ge^{70}Se^{80}}$	0						1.000	1.001	1.003
	25							1.000	1.002
	100							1.000	1.001
	250							1.000	1.001
$\dfrac{Ge^{76}S^{32}}{Ge^{70}S^{32}}$	0							1.000	1.002
	25								1.002
	100								1.001
	250								1.001
$\dfrac{Ge^{76}Te^{130}}{Ge^{70}Te^{130}}$	0								1.000
	25								
	100								
	250								

table and GeF_4 in the left-hand column. The equilibrium constant for the reaction

$$Ge^{70}F_4 + Ge^{76}O^{16} \rightleftharpoons Ge^{76}F_4 + Ge^{70}O^{16}$$

at $25°C$ is 1.024 and is found at the intersection of the GeF_4 row and GeO column. Thus, provided a mechanism for this reaction can be found, a 2.4% germanium isotope effect is predicted and the GeF_4 species will be enriched by 2.4% in the heavier isotope.

For diatomic species, Table III shows the maximum and minimum values to be expected in the ratios of the rate constants in a kinetic isotope effect in which the bond is broken. These were calculated for the different temperatures shown using the Bigeleisen equation (23). In this equation the symmetry numbers cancel because the molecules being considered contain only one atom of the element for which an exchange is being made. The ratio of the transmission coefficients is assumed to be unity. The ratio of the reduced masses of the transition state along the reaction coordinate $\left[\dfrac{m_2^*}{m_1^*}\right]$ is taken to be the ratio of the reduced masses of the two atoms being separated. The minimum kinetic effect occurs when the activated complex behaves like the reactant so that the two $G(u_i)$ terms in the Bigeleisen equation are equal and

TABLE III

Kinetic Isotope Effect-Ratio of Rate Constants k_1/k_2

	Maximum Value of k_1/k_2						
TEMP $^\circ C$	GeS^{32}	$GeSe^{80}$	$GeCl^{35}$	$GeTe^{130}$	GeF^{19}	GeBr	GeO^{16}
0	1.021	1.031	1.018	1.033	1.016	1.026	1.020
25	1.020	1.029	1.017	1.032	1.015	1.025	1.018
100	1.015	1.028	1.016	1.030	1.013	1.024	1.015
250	1.015	1.024	1.015	1.028	1.011	1.023	1.011
	Minimum Value of k_1/k_2						
0	1.013	1.022	1.013	1.027	1.009	1.022	1.007
25	1.013	1.022	1.013	1.027	1.009	1.022	1.007
100	1.013	1.022	1.013	1.027	1.009	1.022	1.007
250	1.013	1.022	1.013	1.027	1.009	1.022	1.007

Subscript 1 refers to Ge^{70}

Subscript 2 refers to Ge^{76}

cancel. In this case the ratio of the rate constants is simply the ratio of the reduced masses and is temperature independent. When the activated complex is like the product the maximum kinetic isotope effect will occur since then the $G(u_i^{\ddagger})\Delta u_i^{\ddagger}$ term is a minimum. ($G(u_i^{\ddagger})\Delta u_i^{\ddagger} = 0$ implies the diatomic bond is completely broken).

The values in the table indicate, for a particular molecule and reaction temperature, how much faster the molecule with the lighter (Ge^{70}) isotope will react than the molecule with the heavier (Ge^{76}) isotope. Hence in the competitive reactions

$$Ge^{70} \ Te^{130} + B + C + \ldots \longrightarrow Ge^{70} + \text{products}$$
$$Ge^{76} \ Te^{130} + B + B + \ldots \longrightarrow Ge^{76} + \text{products}$$
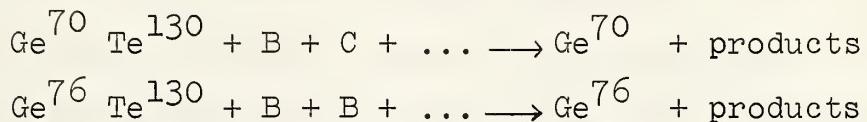
it is predicted that the first reaction will proceed (at the maximum) 3.2% faster than the second reaction at $25^{\circ}C$.

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EXPERIMENTAL

The variation of 0.7% in the natural Ge^{70}/Ge^{76} ratio found by Graham et al (38) and the theoretical predictions of this report suggest the possibility of altering the Ge^{70}/Ge^{76} ratio in laboratory experiments. It was decided, therefore, to try such an experiment and relate it to the theoretical predictions.

Although various equilibria present the possibility of large isotope fractionations as shown in Table II, these seemed difficult to set up experimentally. Kinetic isotope studies, however, seemed tangible and according to Table III, moderate fractionations are expected. The desirable conditions for such an experiment are:

(a) a gaseous reaction or reaction in solution,

(b) a method of halting the reaction at any point,

and (c) the ability to recover the reduced product.

A solution or gaseous reaction is preferable since larger isotope effects are found under these conditions. In contrast, very little isotope fractionation is expected in a solid phase reaction where the process proceeds layer by layer. It is also found that slower reaction rates generally produce

larger isotope effects. In order to measure the kinetic isotope effect, the reaction must be stopped and the isotope ratios determined in the unreduced reactant and reduced product. For these reasons, and others which appear below, a kinetic isotope effect was sought in the reduction of GeO_2 in solution.

A. Chemical Reduction of GeO_2

The following reactions for the reduction of GeO_2 in solution are found in the literature.

(a) reduction with hypophosphorous acid (H_3PO_2) in aqueous solution   (22)

(b) reduction of GeO_2 to GeH_4 (germane) by sodium borohydride ($NaHB_4$)   (62)

(c) reduction of GeO_2 in H_2SO_4 to GeO by the action of zinc powder.   (9)

(c) was rejected because of the possibility of violent localized reactions near the zinc's surface which would yield a negligible isotope effect. (b) is attractive in that the reduced product, germane, is a gas and, therefore, easily separated from the reactants. Germane, however, reacts with oxygen explosively. Therefore, method (a) was chosen. Furthermore, the product GeO is relatively insoluble[*] in comparison

_____

[*]The data available suggest values up to~0.04 gms/100 ml. for GeO as compared to~0.45 gms/100 ml. at 25°C for GeO_2. These values, however, will vary with pH, amount of complexing, etc. in the aqueous solution.

to GeO_2 and can be separated from the reactants as a precipitate.

Dennis and Hulse (22) gave the following method for <u>completely</u> reducing GeO_2 to GeO with H_3PO_2.

GeO_2 is dissolved in 5N-KOH and the solution is acidified to 5N-HCl. An excess of H_3PO_2 is then added and the solution heated at $100^\circ C$ for one hour. Upon neutralization with NH_4OH, a heavy voluminous coloured precipitate of hydrated GeO results. Its colour ranges from a bright orange to a dirty brown depending upon the degree of hydration. This in turn depends upon the pH and temperature of the solution at precipitation.

Since a 10% or less reduction of the GeO_2 was required, the method of Dennis and Hulse had to be altered. Originally, attempts were made to do this by adding only 10% of the stoichiometrically required H_3PO_2 on the assumption that the reaction was

$$2GeO_2 + H_3PO_2 \longrightarrow 2GeO \downarrow + H_3PO_4.$$
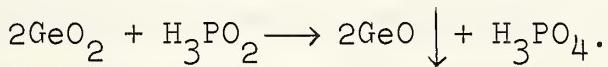
This was unsuccessful as no reduced product was observed, even after hours of heating. Varying the pH and the GeO_2 concentration did not alter this result.

Further searching of the literature revealed the studies on germanium compounds by Everest (29, 32). His reports and private communication (31) indicated that the reduction under

the conditions tried should have occurred, but very slowly.
Further, Everest suggested that in 3-5N-HCl the Ge^{IV} should
be present as un-ionized monomeric GeO_2, but that under these
conditions, any Ge^{II} formed would be immediately complexed by
the HCl. This complexing aids the precipitation of hydrous
GeO upon neutralization.

Since the reduction of GeO_2 by H_3PO_2 is a slow process,
the next approach was to use an excess of H_3PO_2 and to effect
the partial reduction by stopping the reaction at the appropri-
ate time. Preliminary experiments showed that such a method
was feasible and the following procedure was used.

One gram of GeO_2 was dissolved in 500 ml. of H_2O which
was then acidified to ~4.5 N with the addition of 125 ml. of
37% HCl. This solution was heated to the desired reaction
temperature and 25 ml. of H_3PO_2 (preheated to the same tempera-
ture) was added with vigorous stirring. At the proper time[*]
the reaction was halted by quickly neutralizing with NH_4OH.
The solution was then allowed to stand for 4 or 5 hours to
ensure complete precipitation. The hydrous GeO was separated
from the supernatant solution by centrifuging, was washed, and
then recentrifuged to remove soluble ions. After drying, the
precipitate was reoxidized to GeO_2 with HNO_3. Excess nitrogen

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[*](e.g. at $100^{\circ}C$ the reaction time was ~60 secs. for a
10% reduction.)

oxides were removed with the addition of urea by reactions such as

$$(NH_2)_2CO + 2HNO_2 \longrightarrow 2N_2 \uparrow + CO_2 \uparrow + 3H_2O.$$
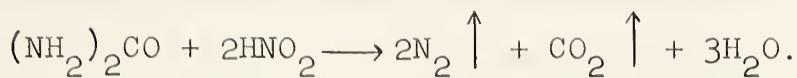
Finally, the solution was heated to dryness to give white crystalline GeO_2 ready for sample preparation.

Biological Investigation: In the introduction, examples were given of isotope fractionation in nature by bacterial reduction. Germanium, although only a trace element, is widely distributed. In the hope that the laboratory reduction studied could be directly related to natural processes, a survey of bacteriological publications was made to ascertain if any organisms participated in germanium reactions. Dr. J. I. Payne of the Provincial Laboratory of Public Health became interested in the project and contributed wholeheartedly to the literature search. No reports were found of bacteria which required germanium in any form for physiological processes. Several accounts are available, however, regarding the absorption of GeO_2 by the fungus "Aspergilus Niger" (37) and at least one report is given on the inhibition of "Escherichi Coli" cultures by 0.01 M GeO_2 (16). Dr. Payne exposed these organisms and also bacteria from a soil·sample to GeO_2. To date, attempts to extract germanium from the organisms have been unsuccessful. However, the presence of germanium in these organisms in very small concentrations cannot be ruled out. Further studies are required in this investigation.

B. Preparation of GeF$_4$

Germanium tetrafluoride gas was chosen for the mass spectrometric analysis of the germanium isotopes because of the simplicity of its mass spectrum and because of the relative ease of its chemical preparation. At N.T.P. germanium tetrafluoride is a colourless gas which fumes strongly on contact with air. It sublimes to a white crystalline solid and the liquid phase does not exist below a pressure of 4 atmospheres. Dry glass is not noticeably attacked by GeF$_4$ but if moisture is present, rapid corrosion results and SiF$_4$ is produced.

Dennis and Laubengayer (23) find the following method the most convenient for preparation of GeF$_4$. The sample in the form of GeO$_2$ is dissolved in 48% HF and the stoichiometric amount of a saturated solution of BaCl$_2$ is added. A white voluminous salt, BaGeF$_6$, immediately precipitates out of solution. The precipitate, which is insoluble in water, is centrifuged, washed thoroughly, and dried at 120°C. It is then decomposed in a vacuum at 700°C to give GeF$_4$ gas and the solid BaF$_2$. Throughout the preparation of BaGeF$_6$ polyethylene beakers and centrifuge tubes are used to prevent silicon contaminants. The advantage of this method of GeF$_4$ preparation is in its chemical simplicity. Further, Reynolds (64) states that this method insures that no isotope fractionation occurs during the sample preparation since all the reactions involved go to completion.

Figure 1 shows the sample preparation line. It was originally constructed with glass stopcocks at (a), (c), (d), and (e) but these were replaced with Hoke valves when it seemed probable that the stopcock grease was introducing moisture and other contaminants into the line. The calibrated furnace is a quartz tube with a removable sheath containing the heating coil. According to Dennis and Laubengayer dry quartz resists corrosion by GeF_4 below $700^{\circ}C$. The remainder of the line is entirely of pyrex glass.

The procedure employed in decomposing the salt $BaGeF_6$ to obtain GeF_4 in the sample preparation line is the following.

Clean, dry $BaGeF_6$ is placed in a quartz tube which is then sealed into the line at point (b). The furnace is slipped over the tube. Valve (a) is then opened and the sample heated to $200^{\circ}C$ until the last traces of moisture have been removed. Valve (a) is now closed and valve (c) opened exposing the sample to the collecting section of the line which has been maintained at high vacuum. All parts of the line are periodically flamed to reduce the moisture content. After thorough evacuation of the system, the sample temperature is raised over a period of 15 minutes to $700^{\circ}C$. As the sample temperature rises past $600^{\circ}C$ and gas begins to evolve, valve (e) is closed. All the gases produced are then frozen down with liquid air around trap 1. After 30 minutes valve (c) is closed and the furnace turned off.

FIG. 1

SAMPLE PREPARATION SYSTEM
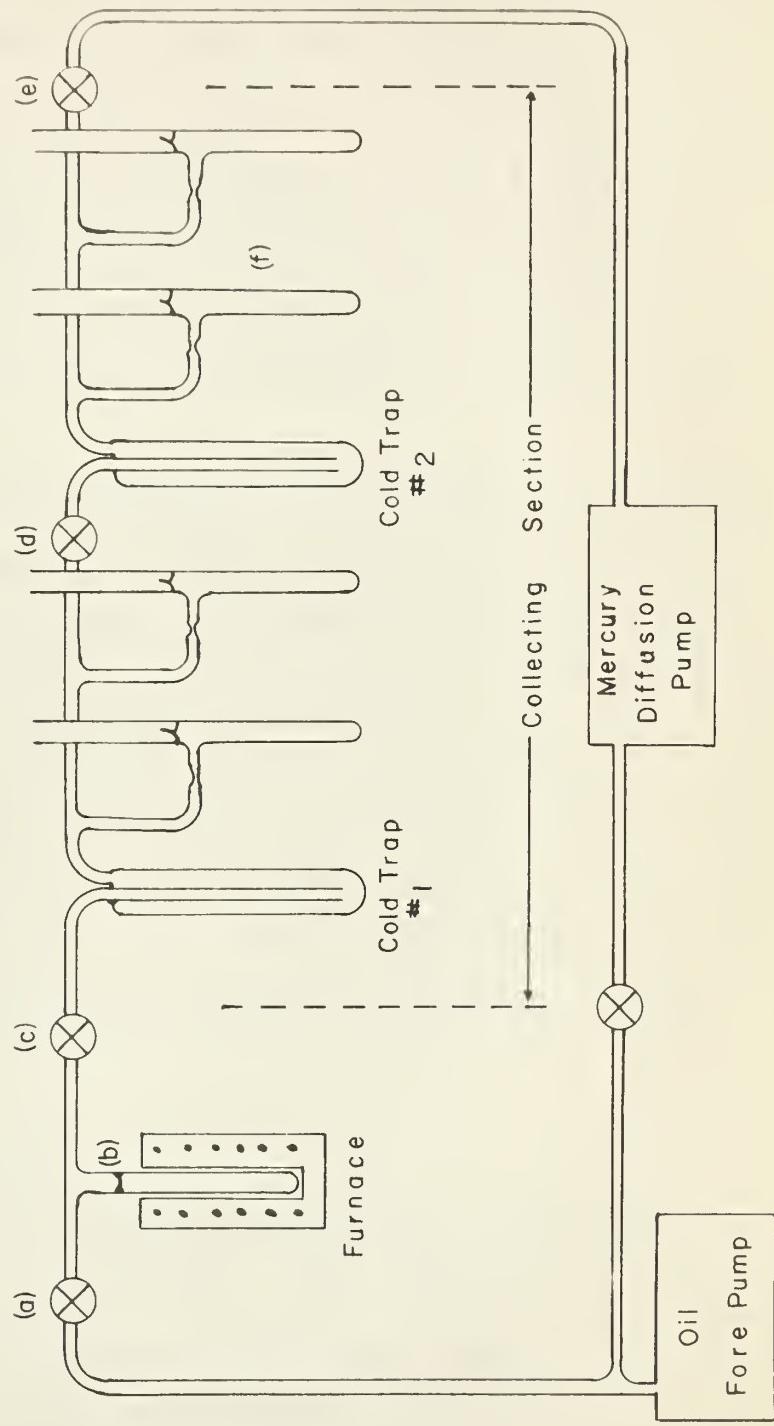
Appropriate freezing baths are next used to separate the GeF_4 from any SiF_4 or HF which may have formed during the decomposition. Figure 2 shows the Clausius-Clapeyron curves of these three gases. It is seen that at about $-45^{\circ}C$ HF has a low vapour pressure while those of SiF_4 and GeF_4 are high. Similarly, at about $-110^{\circ}C$ GeF_4 has a very low vapour pressure in comparison to SiF_4. These temperatures correspond to that of a freezing nitric acid bath and of a freezing ethyl alcohol bath respectively. The following is the method of purification used.

Cold trap 2 is surrounded with a freezing nitric acid bath while one of the break-seal tubes at (f) is partially immersed in an alcohol bath. The liquid air around trap 1 is removed and the white crystals sublimate. Any GeF_4 present is frozen into the break-seal tube in the alcohol bath, while the HF is captured by cold trap 2. The gaseous SiF_4 is then pumped out through (e). If it is felt necessary, this purification can be repeated. Once a clean sample is obtained the break-seal tube containing the GeF_4 is sealed and removed from the line.

C. Mass Spectrometry

The prepared GeF_4 gas was analysed mass spectrometrically to determine the Ge^{70}/Ge^{76} ratio. Two different instruments were used during the course of the investigation. Their features and the studies made with them are now described.

FIG. 2

CURVES of Ln. PRESSURE
vs
RECIPROCAL TEMPERATURE
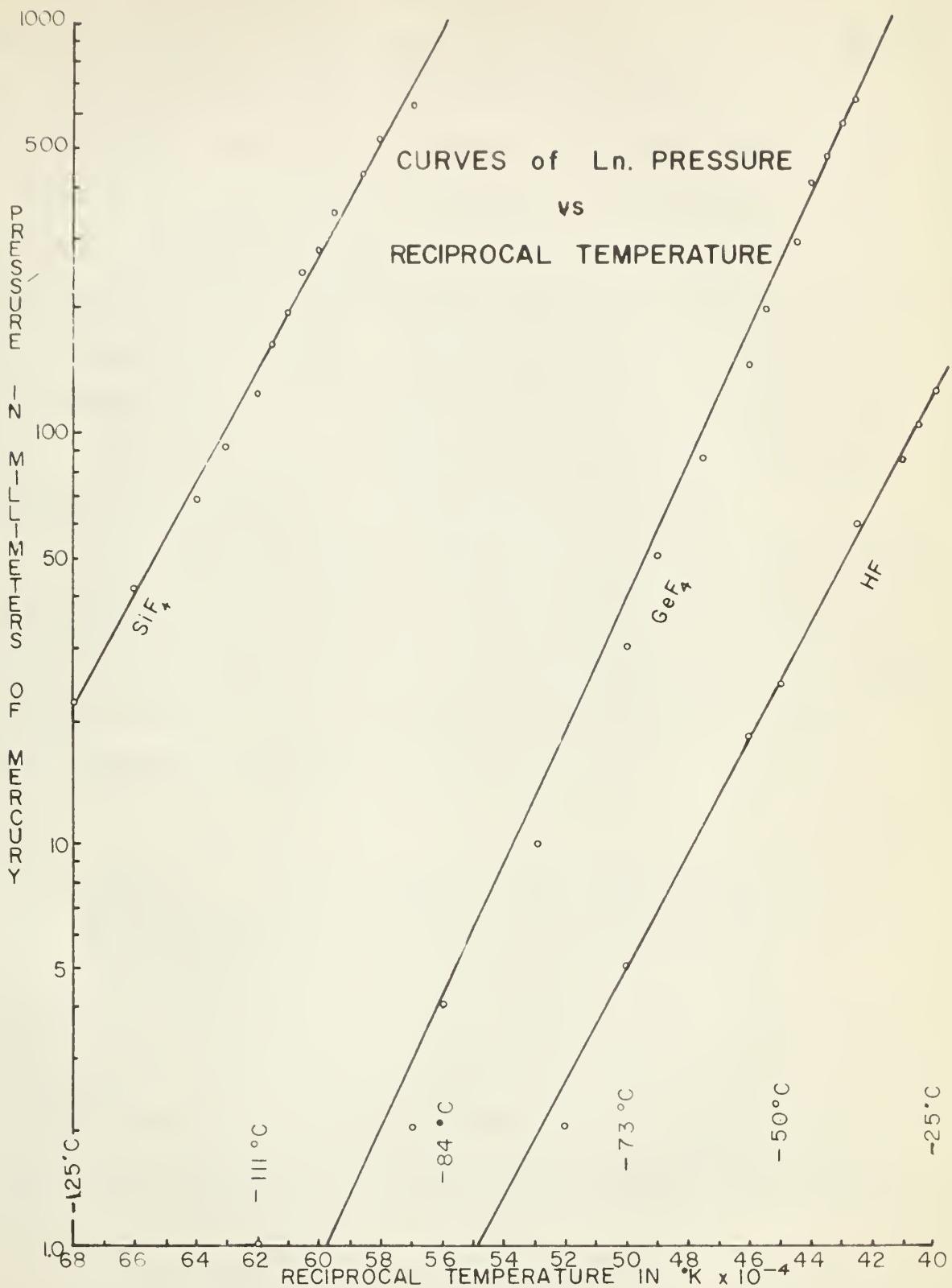
(refs. 18, 23, 63)

The first instrument employed a 6-inch radius, 60° magnetic analyser to separate ion currents of different masses. GeF_4 molecules were ionized by an electron beam travelling normally to the inlet flow direction. The ions formed were then linearly accelerated by a potential difference of 2000 volts and subsequently separated in the magnetic field. Ion currents of different masses were introduced into the collector slit by magnetic scanning. Those collected were amplified and displayed as "peaks" (Figure 6) on a continuous recording chart. The relative peak heights were measured to determine the relative abundances of the germanium isotopes.

In the ionizing process, GeF_4 splits into many singly and doubly charged ions. The GeF_3^+ ion is found in the greatest abundance (over 80%) and is used in abundance analysis. Graham et al (38) reported the following distribution for singly ionized species with 80 e.v. electrons.

Ion	GeF_4^+	GeF_3^+	GeF_2^+	GeF^+	Ge^+
% Abundance	1.8	86.8	1.8	2.6	7.0

Since fluorine has only one stable isotope, F^{19}, all of these spectra yield directly the abundances of the germanium isotopes. Since this distribution was expected to vary with electron energy, the electronics of the mass spectrometer was adapted

to permit a study of the abundances as a function of different electron energies from 40 e.v. to 100 e.v. The results are shown graphically in Figure 3. It is observed that with increased electron energy, there is a greater percentage of doubly charged ions formed at the expense of the singly charged ones. The results seem rational because more energy is required to form the doubly charged ions, but a quantitative description is difficult. A graph of the type shown is beneficial for finding the optimum condition for the production of a particular ion and, inversely, such information can be used to subdue known contaminant ions. The results of Graham et al are consistent with this graph but, in general, slight differences might arise with various instruments and conditions.

A sample handling system was built (Figure 4) which made it possible to compare two samples of GeF_4 in the mass spectrometer under identical conditions. Metal Hoke valves were again used to eliminate contaminations. The two large bulbs served as storage units for identical amounts of each sample. Their contents were matched in terms of the ion currents which were produced in the mass spectrometer.

The "run" procedure consisted of admitting one of the samples and tracing 22 complete spectra of the GeF_3^+ ion species. This sample was stored while the other sample was similarly examined. Typically, a run consisted of 3 or 4 such comparisons.

FIG. 3

PERCENTAGE OF TOTAL IONS PRESENT
FOR DIFFERENT IONIZATION POTENTIALS

GeF_4
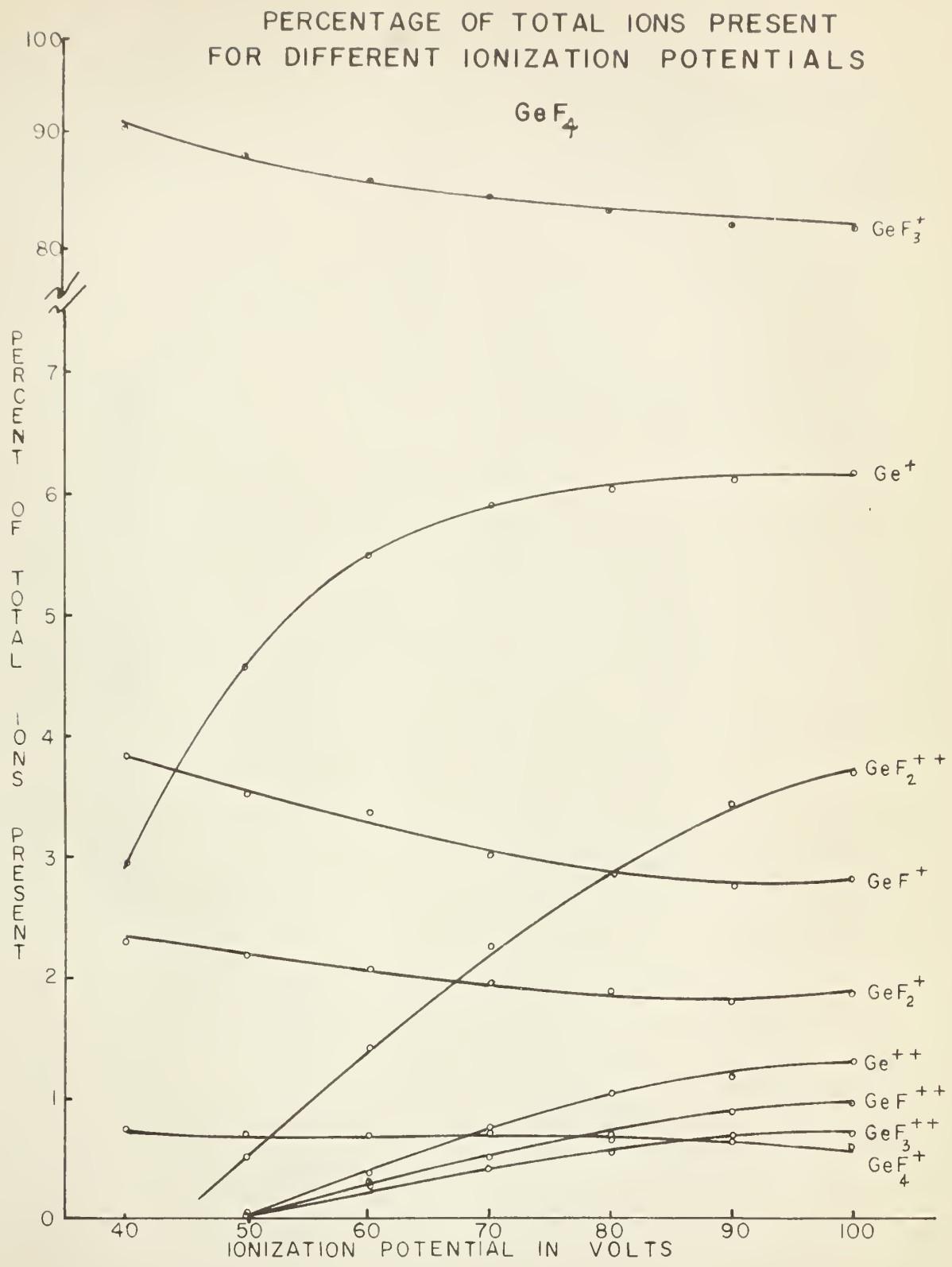
FIG. 4

SAMPLE INLET SYSTEM
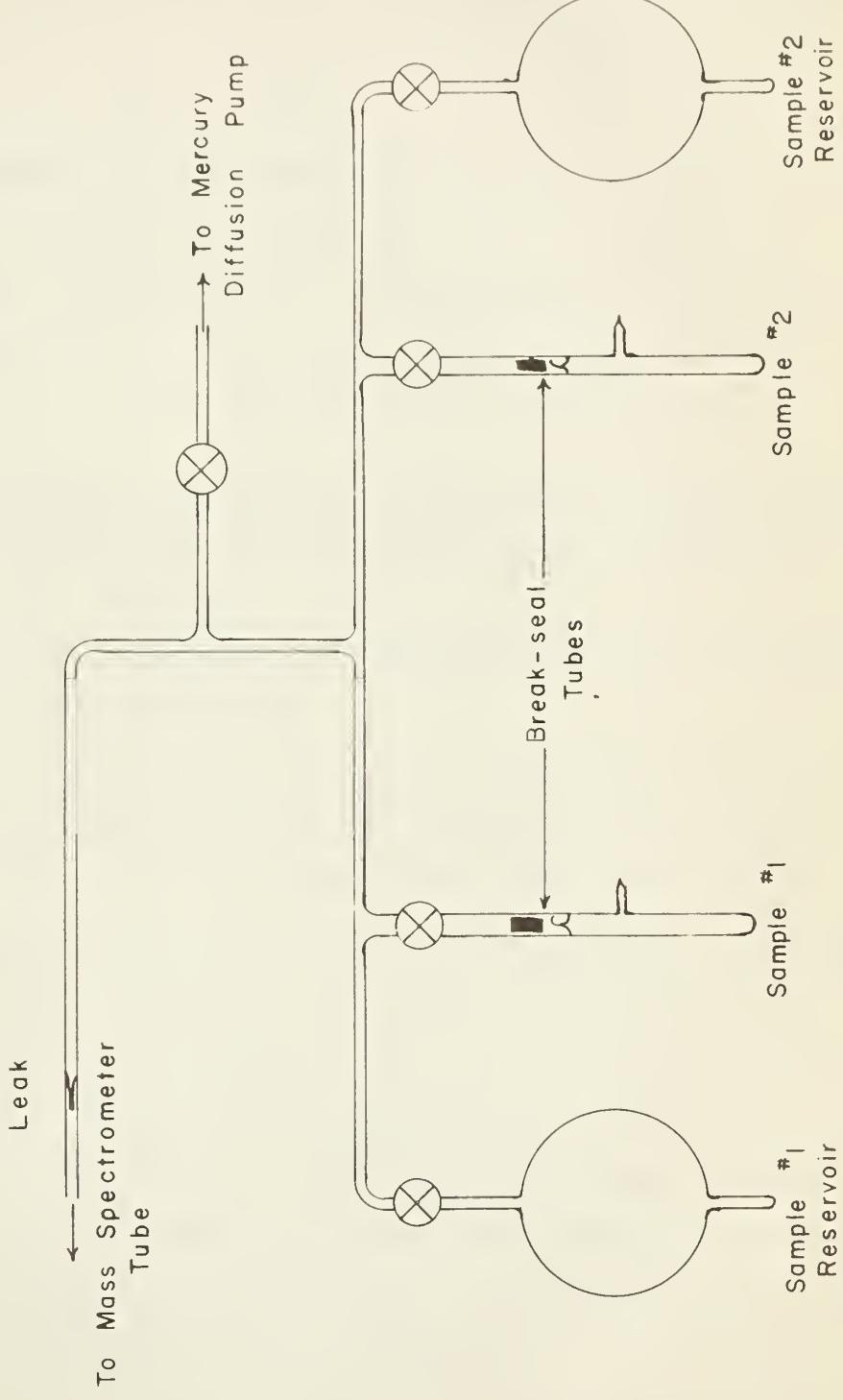
The second mass spectrometer was basically similar to the
first with the exception of a larger magnetic analyser (12-inch
radius, 90°). It was also equipped to collect simultaneously
the $Ge^{70}F_3^+$ and $Ge^{76}F_3^+$ ion currents and compare them by a
null technique as shown in Figure 5. The larger current i_1
produces a greater voltage across resistance R_1 than that of
i_2 across an identical resistance R_2. R_1 is a precision
direct-reading potentiometer. Its setting for a null reading
of the recorder gives directly the voltage ratio V_2/V_1 and,
therefore, i_2/i_1. The advantages of such a system are:

1. Recording is continuous in contrast to single collec-
   tion where data is recorded for only a fraction of
   the total run time.

2. Laborious measurement of peak heights and associated
   errors are eliminated.

3. Since the ratio is recorded, fluctuations in the mass
   spectrometer source do not limit the precision to
   the same extent as single collection techniques.

Single collection traces for the 12-inch instrument are shown
in Figure 6. The flat tops of the peaks indicate that the
ion beam is narrow as compared to the collector slit widths.
This is desirable for successful simultaneous collection.

An additional feature on this instrument was a magnetic
valve system, as described by Wanless and Thode (87), which
allowed two samples to be alternately introduced into the mass
spectrometer within one minute intervals.

FIG. 5

SIMULTANEOUS   COLLECTION
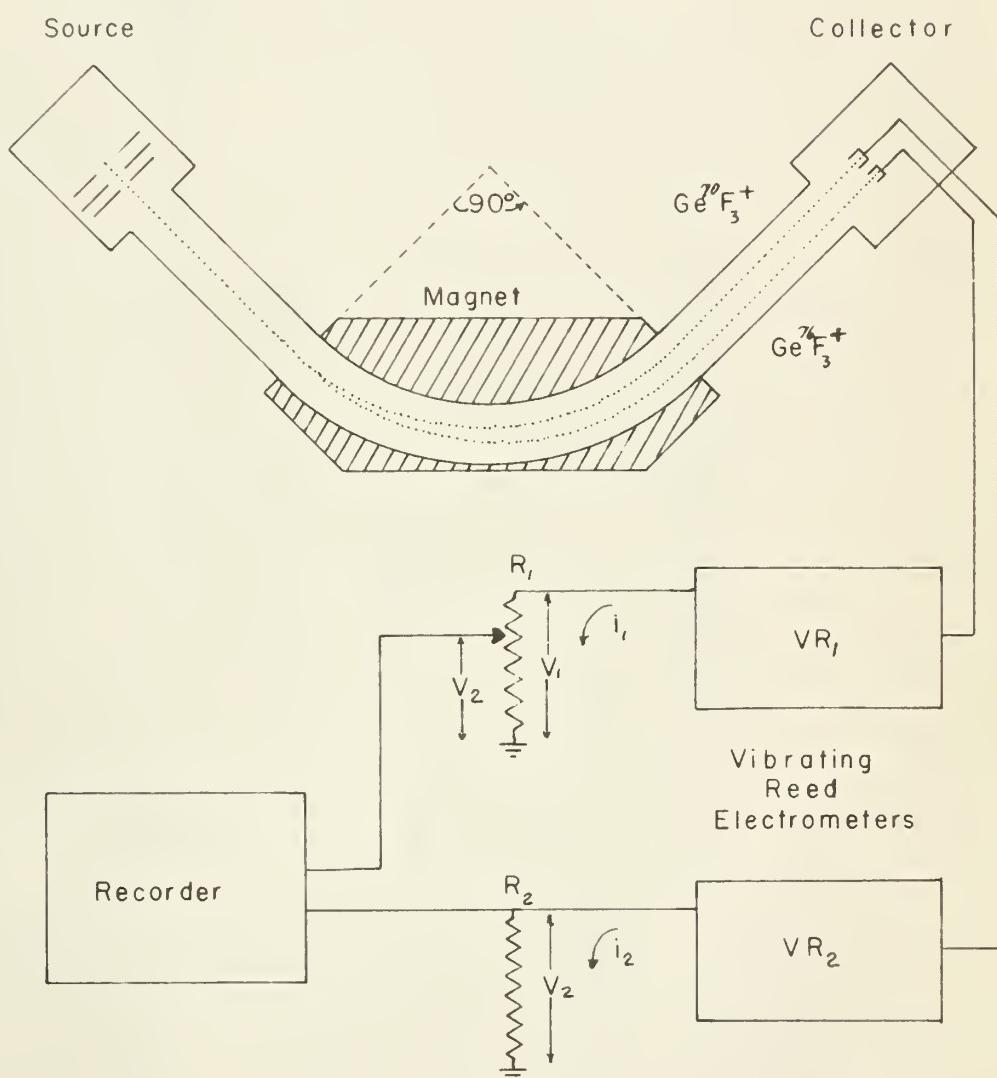
FIG. 6

SINGLE COLLECTION TRACES
WITH 12" RADIUS MASS SPECTROMETER

WIDE COLLECTOR SLIT
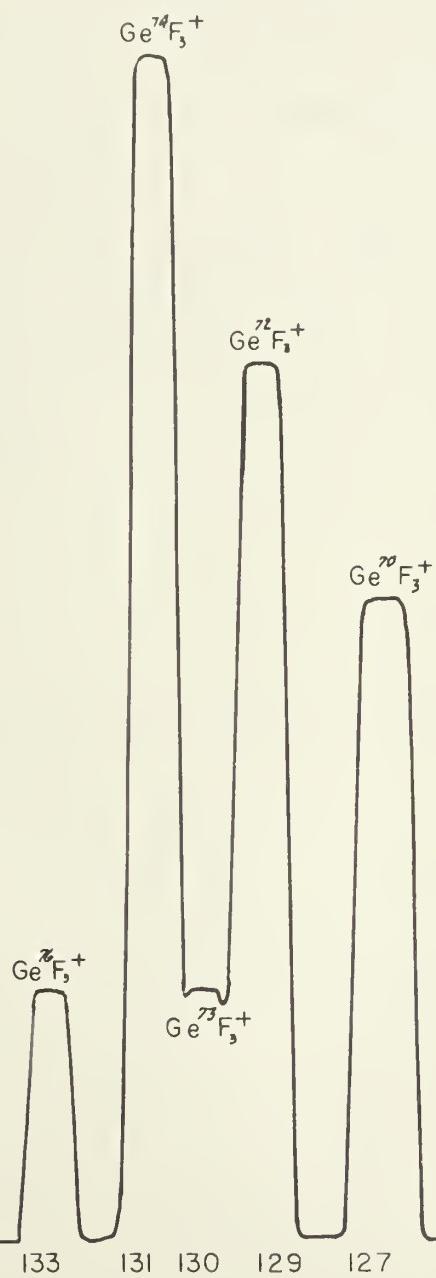
NARROW COLLECTOR SLIT
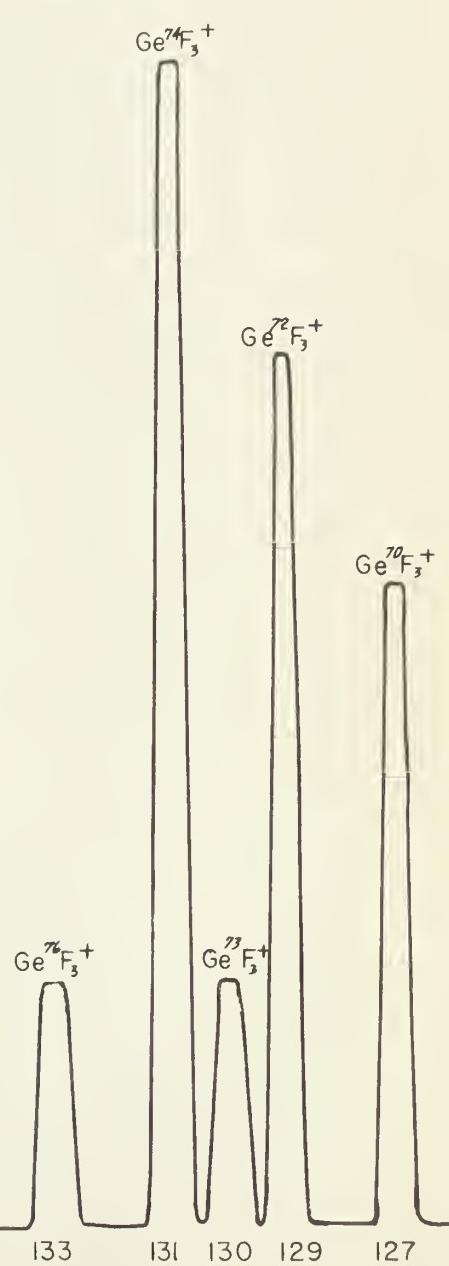
In the early stages of the experimental study, contaminants presented a problem. Under some conditions, it appeared from the mass spectra that the compound $GeOF_2$ (germanium oxyfluoride) was produced. A literature search did not reveal any reports of this compound although the analagous $GeOCl_2$ has received study. In the quoted results, this contamination was less than 0.1% and its contribution to any measured ion currents was undetectable. SiF_4 contamination was present in a low percentage in spite of the purification procedures, but its spectra was outside of the mass range studied. Since runs on the first instrument lasted as long as 15 hours with the results remaining consistent, it was felt that contaminant effects were non-existent.

RESULTS OF EXPERIMENTAL STUDY

As an overall check on the reduction study, samples of GeO_2 were completely reduced to GeO and completely reoxidized. These samples were compared mass spectrometrically to non-reduced GeO_2. Two such "runs" were made by single collection and these showed that the processed and non-processed GeO_2 were identical in their isotopic composition to within 0.2% (probably the precision of the instrumentation).

Two independent partial reductions of GeO_2 were carried out at $100^{o}C$. The reduced and non-reduced germanium were compared mass spectrometrically by single collection. Between one hundred and two hundred traced spectra of each reduction gave the result

$$\frac{Ge^{70}/Ge^{76} \text{ reduced portion}}{Ge^{70}/Ge^{76} \text{ unreduced portion}} = 1.010 \pm 0.002_5.$$

An additional partial reduction at $100^{o}C$ was examined with the 12-inch radius mass spectrometer by simultaneous collection and $\dfrac{Ge^{70}/Ge^{76} \text{ reduced portion}}{Ge^{70}/Ge^{76} \text{ unreduced portion}}$ was found to be $1.012 \pm 0.001_5$.

Discussion

The results of the theoretical study as summarized in Table II predict that isotope fractionations of as much as 3.5% are expected in equilibrium Ge^{70} - Ge^{76} exchange reactions. Table III predicts maximum kinetic isotope effects of the same order for the breaking of diatomic bonds.

The experimental partial reduction of GeO_2 yielded a product enriched in the lighter isotope Ge^{70} by about 1.2%. Since the amount of GeO_2 reduced was less than 10%, the value 1.012 is close to the ratio of the rate constants k_1/k_2 (13) for

$$Ge^{70}O_2 \xrightarrow{k_1} Ge^{70}O$$

$$Ge^{76}O_2 \xrightarrow{k_2} Ge^{76}O$$
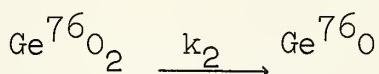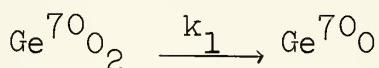
Since, according to Everest (31), GeO_2 existed as the monomer in the reaction solution, it would have been desirable to have the appropriate vibrational frequencies. Data for monomeric GeO_2 is not available, and, therefore, an ideal model for theoretical calculations cannot be constructed.

Since the germanium is significantly heavier than the oxygen atom, an approximate model is used to describe the reaction, viz. a simple diatomic Ge-O bond being completely broken. Table III shows that the minimum and maximum k_1/k_2

ratios expected on the basis of this model are 1.007 and 1.015 respectively at $100^{\circ}C$. The experimental value 1.012 falls within these limits, but such a simple model cannot give any information concerning the activated complex of the GeO_2 reduction.

Although the laboratory reduction was not correlated directly to natural processes, the result is important because it verifies theoretical predictions and represents original research of this type with the element germanium.

APPENDIX A

CALCULATION OF ISOTOPIC VIBRATIONAL FREQUENCY SHIFTS

For a number of germanium-containing compounds and species, values of the normal vibrational frequencies are available in the literature. These values were assumed to apply to the most abundant germanium isotope Ge^{74} and the frequencies of the Ge^{70} and Ge^{76} molecules were then calculated from these known frequencies using normal force equations of the molecule's particular symmetry type.

A. Diatomic Molecules

In finding the isotopic frequencies for diatomic molecules an anharmonic oscillator model for the molecule is chosen. This model has a potential energy function of the form

$$U = f(r - r_e)^2 - g(r - r_e)^3 + \ldots \qquad (1)$$

where r_e is the equilibrium internuclear distance and $(r - r_e)$ is the displacement from this equilibrium position. The Shroedinger equation is then

$$\nabla^2 \psi + \frac{8\pi^2 \mu}{h^2} (E - U)\psi = 0$$

Provided the anharmonicity is small $(g \ll f)$ the eigenvalues of this equation will be given by

$$E_v = hc \left[\omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 \ldots \right]$$

(2)

These are the energy levels where v is the vibrational quantum number, ω_e the classical vibrational frequency in cms^{-1}, and μ the reduced mass. An harmonic oscillator has a classical vibration frequency given by

$$V_{osc} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \text{ secs}^{-1}$$

where it is acting under a restoring force of $-K(r - r_e)$ during a displacement of $(r - r_e)$. Since the potential energy curves of isotopic molecules are identical to a high degree, we may assume that K is independent of the isotope. Thus the classical frequency of an isotopic molecule is given in terms of the vibrational frequency of the more abundant molecule by

$$V_i = V_{osc}\sqrt{\frac{\mu}{\mu_i}} = \rho V_{osc}$$

(3)

and since $V = c\omega_e$

$$(\omega_e)_i = \rho\omega_e$$

(4)

From (2) and (4) the energy levels of the isotopic molecule may now be written as

$$(E_v)_i = hc \left[\rho \omega_e (v + 1/2) - \rho^2 \omega_e x_e (v + 1/2)^2 + \ldots \right] \qquad (5)$$

The energy change in a vibrational transition (where the selection rule is $\Delta v = \pm 1$) in going from $v = 0$ to $v = 1$ is given by equation (2):

$$\Delta E_v = hc \left[\omega_e - 2 \omega_e x_e + \ldots \right] \qquad (6)$$

$$= hc\omega$$

When written in terms of the isotopic classical vibrational frequencies, equation (6) becomes

$$(\Delta E_v)_i = hc \left[\rho \omega_e - 2\rho^2 \omega_e x_e + \ldots \right] \qquad (7)$$

$$= hc\omega_i$$

Finally, from equation (7) the vibrational frequency of the isotopic molecule can be written in terms of the frequency of the more abundant molecule as

$$\omega_i = \rho \omega_e - 2\rho^2 \omega_e x_e + \ldots \qquad (8)$$

The calculation of the vibrational frequencies of Ge^{70} and Ge^{76} containing diatomic species then proceeds as follows. From Herzberg (43), experimental values of ω_e and

$\omega_e x_e$, assumed to apply to the Ge^{74} containing molecule, are
obtained. One evaluates

$$\omega_e^{70} = \left[\frac{\mu^{74}}{\mu^{70}}\right]^{1/2} \cdot \omega_e^{74} = \rho^{70} \, \omega_e^{74}$$

$$\omega_e^{76} = \rho^{76} \, \omega_e^{74}$$

and similarly

$$(\omega_e x_e)^{70} = \left[\rho^{70}\right]^2 (\omega_e x_e)^{74}$$

$$(\omega_e x_e)^{76} = \left[\rho^{76}\right]^2 (\omega_e x_e)^{74}.$$

Now from these values and using equation (8),

$$\omega^{70} = \omega_e^{70} - 2(\omega_e x_e)^{70}$$

$$\omega^{76} = \omega_e^{76} - 2(\omega_e x_e)^{76}.$$

For the data which were available the calculations for Ge^{70}
and Ge^{76} containing diatomic species are shown in Table IV.

B. <u>Polyatomic Molecules</u>

To calculate the isotopic vibrational frequencies of a
polyatomic molecule, it is necessary to have detailed informa-
tion about the structure of the molecule so that equations
can be set up which describe the molecular force fields. For
molecules of a particular symmetry type, several sets of force

TABLE IV

Calculation of Vibrational Frequency Shifts for Ge^{70} and Ge^{76} Containing Molecules

MOLECULE	ω_e^{74} cms^{-1}	$(\omega_e x_e)^{74}$ cms^{-1}	$\frac{\mu^{74}}{\mu^{70}}$	$\left[\frac{\mu^{74}}{\mu^{70}}\right]^{\frac{1}{2}}$	$\frac{\mu^{74}}{\mu^{76}}$	$\left[\frac{\mu^{74}}{\mu^{76}}\right]^{\frac{1}{2}}$	ω_e^{70} cms^{-1}	ω_e^{76} cms^{-1}	$(\omega_e x_e)^{70}$ cms^{-1}	$(\omega_e x_e)^{76}$ cms^{-1}	ω^{70} cms^{-1}	ω^{76} cms^{-1}
GeS^{32}	575.8	1.80	1.017	1.009	0.992	0.996	580.8	573.5	1.83	1.79	577.1	569.9
$GeSe^{80}$	406.8	1.20	1.030	1.015	0.986	0.993	412.8	403.9	1.24	1.18	411.6	401.6
$GeCl^{35}$	407.6	1.36	1.018	1.009	0.992	0.996	411.3	405.9	1.39	1.35	408.5	403.2
$GeTe^{130}$	323.4	1.00	1.036	1.018	0.983	0.992	329.2	320.7	1.04	0.98	327.2	318.7
GeF	665.2	2.79	1.012	1.006	0.995	0.997	669.1	663.4	2.82	2.77	663.5	657.9
$GeBr$	296.6	0.90	1.030	1.015	0.986	0.993	301.0	294.6	0.93	0.89	299.1	292.8
GeO^{16}	985.7	4.30	1.010	1.005	0.995	0.998	990.7	983.4	4.34	4.28	982.0	974.8

equations often exist depending upon the molecular model used. In the calculations below, the set of force equations in the literature which seemed to best describe the molecule were chosen.

Some of the frequencies which result from theoretical calculations differ slightly from the observed frequencies. Since the Bigeleisen-Mayer function $G(u_i)$ depends on the absolute frequency, it seemed desirable to align the calculated Ge^{74} frequencies with the observed ones. This was approximated by a linear correction.

All of the polyatomic molecules considered were of tetrahedral structure. There are four normal modes of vibration associated with molecules of this symmetry type; a non-degenerate mode (ω_1) of symmetry type A_1, a doubly degenerate mode (ω_4) of type E, and two triply degenerate modes $(\omega_2$ and $\omega_3)$ of symmetry type F_2. These normal vibrations are shown in Figure 7.

$GeCl_4$

Heath and Linnett (41) have studied the application of two different force fields to tetrahedral XY_4 molecules and, along with several other compounds, considered $GeCl_4$. They found that the "Orbital Valency Force Field" equations with an added term to represent the interaction of the non-bonded atoms were superior to the "Simple Valency Force Field"

FIG.7

NORMAL VIBRATIONS
of a
TETRAHEDAL XY₄ MOLECULE

ν_1

A_1

ν_{2a}

ν_{2b}

E

ν_{3a}

ν_{3b}

ν_{3c}

F_2

ν_{4a}

ν_{4b}

ν_{4c}

F_2

(ref. 44, p. 100)
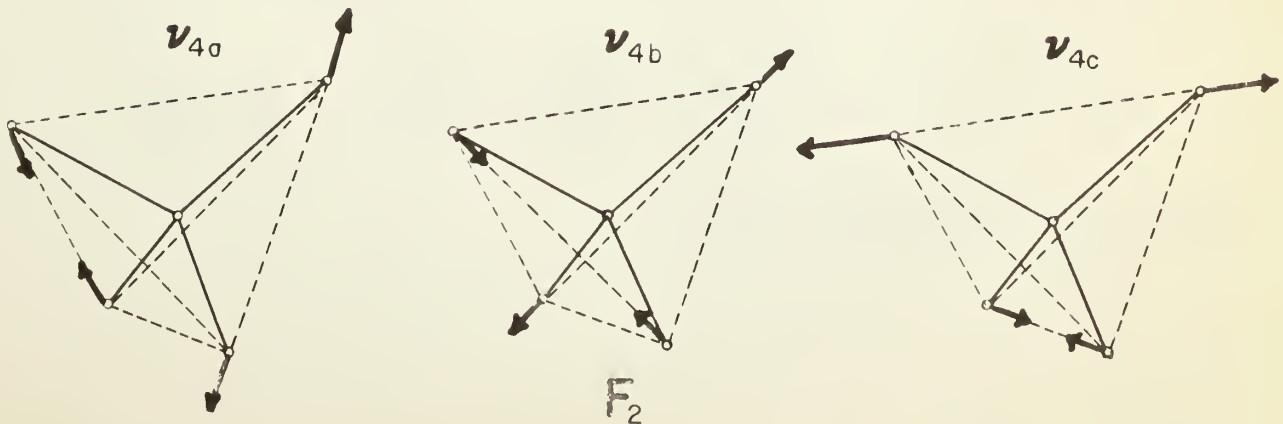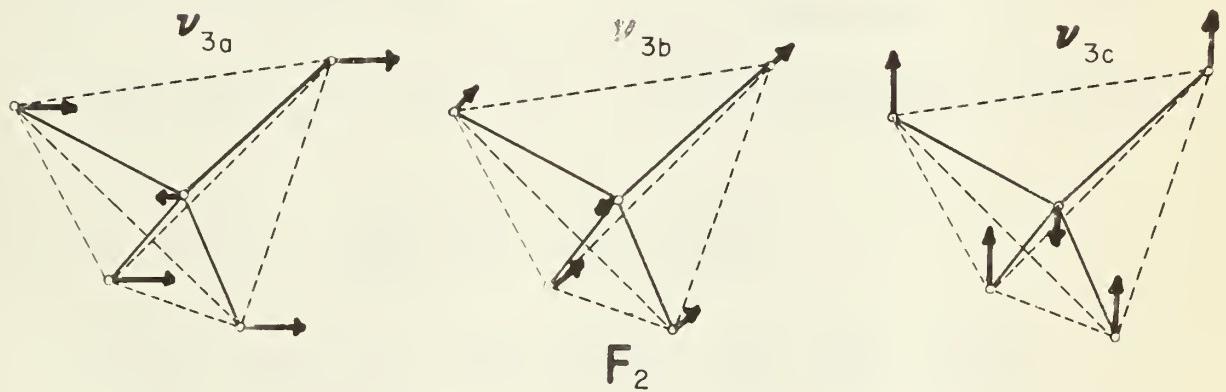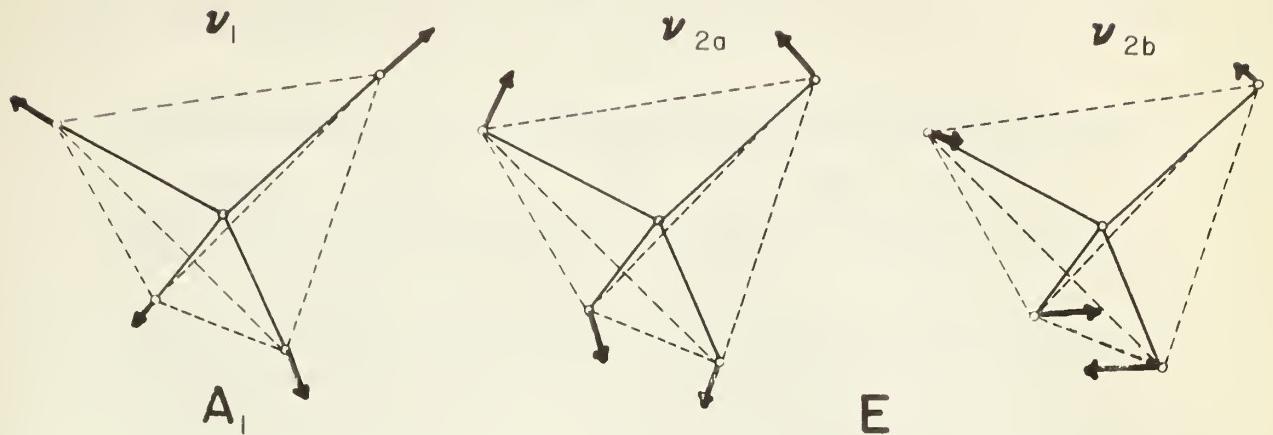
equations with a similar term added. The following table shows
the agreement between observed and calculated frequencies
using the Orbital Valency Force Field (O.V.F.F.) for $GeCl_4$.

$GeCl_4$	ω_1	ω_2	ω_3	ω_4
observed frequencies	397 cms^{-1}	451 cms^{-1}	171 cms^{-1}	132 cms^{-1}
calculated frequencies	397 cms^{-1}	454 cms^{-1}	170 cms^{-1}	132 cms^{-1}

Heath and Linnett give the following force equations and
constants for $GeCl_4$ using the O.V.F.F. approach.

$$\lambda_1 = \frac{1}{m_2}\left[k_1 + 8A\right] \qquad (1)$$
(non-degenerate vibration)

$$\lambda_4 = \frac{1}{m_2}\left[k_d' + 2A + \frac{B}{R}\right] \qquad \text{(doubly degenerate vibration)} \qquad (2)$$

$$\lambda_2 + \lambda_3 = \left[\frac{1}{m_2} + \frac{4}{3m_1}\right]\left[k_1 + \frac{8A}{3} - \frac{4}{3}\frac{B}{R}\right]$$

$$+ \left[\frac{1}{m_2} + \frac{8}{3m_1}\right]\left[k_d' + \frac{4A}{3} + \frac{10}{3}\frac{B}{R}\right] - \frac{8}{3m_1}\left[\frac{8A}{3} - \frac{4}{3}\frac{B}{R}\right]$$

$$\lambda_2\lambda_3 = \left[\frac{1}{m_2^2} + \frac{4}{m_1 m_2}\right]\left\{\left[k_1 + \frac{8A}{3} - \frac{4}{3}\frac{B}{R}\right]\right.$$

$$\cdot \left[k_d' + \frac{4}{3}A + \frac{10}{3}\frac{B}{R}\right] - \frac{1}{2}\left[\frac{8}{3}A - \frac{4}{3}\frac{B}{R}\right]^2 \right\} \qquad (3)$$

(triply degenerate vibrations)

where $\lambda_1 = 4\pi^2 c^2 \omega_1^2$ ω_1 = frequency in cms^{-1}

m_1 = mass of germanium atom

m_2 = mass of chlorine atom

k_1 = the bond stretching constant of the Ge - Cl bond

$r^2 k_\alpha'$ = the angle bending constant of the Cl - Ge - Cl angle

r = the Ge - Cl bond length.

-B and 2A are the first and second differentials of the potential energy function representing the repulsion between the non-bonded atoms. The constants have the following values for GeCl$_4$.

$$k_1 = 2.44 \quad \text{x } 10^5 \text{ dynes/cm.}$$
$$k_\alpha' = 0.147 \quad \text{x } 10^5 \text{ dynes/cm.}$$
$$A = 0.10 \quad \text{x } 10^5 \text{ dynes/cm.}$$
$$\frac{B}{R} = 0.0154 \text{ x } 10^5 \text{ dynes/cm.}$$

If the frequencies are in cms^{-1} and the masses in atomic mass units (A.M.U.), then $\lambda_1 = 5.8894 \times 10^{-2} \omega_1^2$. It is noted that λ_1 and λ_4 are independent of the mass of the germanium atom so that they remain unchanged with isotopic substitution of germanium. $\lambda_2 + \lambda_3$ and $\lambda_2 \lambda_3$ are next found from equations (3) for a particular germanium isotope. Subsequently λ_2 and λ_3 and then ω_2 and ω_3 can be found by using

$$\lambda^2 - (\lambda_2 + \lambda_3)\lambda + \lambda_2 \lambda_3 = 0$$

whose roots are given by

$$2\lambda_2 = (\lambda_2 + \lambda_3) + \sqrt{(\lambda_2 + \lambda_3)^2 - 4\lambda_2\lambda_3}$$

$$2\lambda_3 = (\lambda_2 + \lambda_3) - \sqrt{(\lambda_2 + \lambda_3)^2 - 4\lambda_2\lambda_3}$$

The values of ω_2 and ω_3 are found to be as follows.

	$\lambda_2 + \lambda_3$	$\lambda_2\lambda_3$	ω_2	ω_3
$Ge^{70}Cl_4$	$1.3943 \times 10^4 secs^{-2}$	$2.0660 \times 10^7 secs^{-4}$	$456.0 \ cms^{-1}$	$169.3 \ cms^{-1}$
$Ge^{74}Cl_4$	$1.3649 \times 10^4 secs^{-2}$	$1.9915 \times 10^7 secs^{-4}$	$451.1 \ cms^{-1}$	$168.4 \ cms^{-1}$
$Ge^{76}Cl_4$	$1.3514 \times 10^4 secs^{-2}$	$1.9570 \times 10^7 secs^{-4}$	$448.6 \ cms^{-1}$	$167.3 \ cms^{-1}$

If the frequencies calculated for $Ge^{74}Cl_4$ are compared with the observed frequency, a discrepancy is noted.

	ω_2	ω_3
$Ge^{74}Cl_4$ observed	$451 \ cms^{-1}$	$171 \ cms^{-1}$
$Ge^{74}Cl_4$ calculated	$451.1 \ cms^{-1}$	$168.4 \ cms^{-1}$

Therefore correction factors of $\left[\dfrac{451}{451.1}\right]$ for frequency ω_2 and $\left[\dfrac{171}{168.4}\right]$ for frequency ω_3 are applied to the calculated values for Ge^{70} and Ge^{76} to align their values with the observed value for Ge^{74}. The normal frequencies are then

	ω_1	ω_2	ω_3	ω_4
$Ge^{70}Cl_4$	397 cms^{-1}	455.8 cms^{-1}	171.9 cms^{-1}	132 cms^{-1}
$Ge^{76}Cl_4$	397 cms^{-1}	448.5 cms^{-1}	169.8 cms^{-1}	132 cms^{-1}

GeBr$_4$

Heath and Linnett (41) give constants for the O.V.F.F. description of GeBr$_4$ since they found that the Orbital Valency Force Field is superior to the Simple Valency Force Field for this molecule also. They list the constants for the normal force equations as

$$k_1 = 1.95 \quad \times 10^5 \text{ dynes/cm.}$$

$$k_d' = 0.115 \quad \times 10^5 \text{ dynes/cm.}$$

$$A = 0.080 \quad \times 10^5 \text{ dynes/cm.}$$

$$\frac{B}{R} = 0.0123 \times 10^5 \text{ dynes/cm.}$$

The equations and method of solution for this molecule are similar to those given for GeCl$_4$. The values of ω_2 and ω_3 are found to be

	$\lambda_2 + \lambda_3$	$\lambda_2\,\lambda_3$	ω_2	ω_3
$Ge^{70}Br_4$	$7.3645 \times 10^3 cms^{-2}$	$4.7521 \times 10^6 secs^{-4}$	$335.9\ cms^{-1}$	$110.3\ cms^{-1}$
$Ge^{74}Br_4$	$7.1295 \times 10^3 cms^{-2}$	$4.5414 \times 10^6 secs^{-4}$	$330.4\ cms^{-1}$	$109.6\ cms^{-1}$
$Ge^{76}Br_4$	$7.0214 \times 10^3 cms^{-2}$	$4.4444 \times 10^6 secs^{-4}$	$327.5\ cms^{-1}$	$109.2\ cms^{-1}$

Since we have assumed that the observed frequencies are due to the most abundant Ge^{74} isotope, the frequencies calculated for $Ge^{74}Br_4$ and the observed ones should coincide. A discrepancy is noted, however.

	ω_2	ω_3
$Ge^{74}Br_4$ observed	$328\ \ \ cms^{-1}$	$111\ \ \ cms^{-1}$
$Ge^{74}Br_4$ calculated	$330.4\ cms^{-1}$	$109.6\ cms^{-1}$

A correction factor of $\left[\dfrac{328}{330.4}\right]$ for frequency ω_2 and $\left[\dfrac{111}{109.6}\right]$ for frequency ω_3 is then applied to the values calculated for the isotopic molecules $Ge^{70}Br_4$ and $Ge^{76}Br_4$ to align their values with the observed ones for $Ge^{74}Br_4$. Finally the normal isotopic frequencies are:

	ω_1	ω_2	ω_3	ω_4
$Ge^{70}Br_4$	$234\ cms^{-1}$	$333.5\ cms^{-1}$	$111.7\ cms^{-1}$	$78\ cms^{-1}$
$Ge^{76}Br_4$	$234\ cms^{-1}$	$325.1\ cms^{-1}$	$110.6\ cms^{-1}$	$78\ cms^{-1}$

GeF$_4$

For this molecule, the force constants of the O.V.F.F. equations of Heath and Linnett (41) have been calculated by Caunt, Short, and Woodward (17) who give the following values.

$$k_1 = 5.17 \quad \text{x } 10^5 \text{ dynes/cm.}$$

$$k_d^! = 0.222 \quad \text{x } 10^5 \text{ dynes/cm.}$$

$$A = 0.115 \quad \text{x } 10^5 \text{ dynes/cm.}$$

$$\frac{B}{R} = 0.0177 \text{ x } 10^5 \text{ dynes/cm.}$$

These authors have taken the observed GeF$_4$ frequencies to be:

$$\omega_1 = 738 \text{ cms}^{-1} \qquad \omega_3 = 260 \text{ cms}^{-1}$$

$$\omega_2 = 800 \text{ cms}^{-1} \qquad \omega_4 = 205 \text{ cms}^{-1}$$

Since the method of calculation is exactly the same as with the preceding two molecules only the results are given.

	$\lambda_2 + \lambda_3$	$\lambda_2\lambda_3$	ω_2	ω_3
Ge^{70}F$_4$	4.1745 x 10^4 secs^{-2}	1.3352 x 10^8 secs^{-4}	805.9 cms^{-1}	243.5 cms^{-1}
Ge^{74}F$_4$	4.1161 x 10^4 secs^{-2}	1.2976 x 10^8 secs^{-4}	800.3 cms^{-1}	241.6 cms^{-1}
Ge^{76}F$_4$	4.0891 x 10^4 secs^{-2}	1.2803 x 10^8 secs^{-4}	797.8 cms^{-1}	240.8 cms^{-1}

Again a discrepancy is found between the calculated and observed frequencies for Ge^{74}F$_4$.

	ω_2	ω_3
Ge^{74}F$_4$ observed	800 cms^{-1}	260 cms^{-1}
Ge^{74}F$_4$ calculated	800.3 cms^{-1}	241.6 cms^{-1}

When this has been corrected the final normal frequencies are then:

	ω_1	ω_2	ω_3	ω_4
$Ge^{70}F_4$	738 cms^{-1}	805.6 cms^{-1}	262.0 cms^{-1}	205 cms^{-1}
$Ge^{76}F_4$	738 cms^{-1}	797.5 cms^{-1}	259.1 cms^{-1}	205 cms^{-1}

GeH_4

For this tetrahedral molecule Heath, Linnett, and Wheatley (42) have calculated the constants for a slightly different set of force equations. These are the Orbital Valency Force Field equations combined with the idea of "orbital following" which were developed by Linnett and Wheatley (52). The observed frequencies were taken to be:

$$\omega_1 = 2090 \text{ cms}^{-1} \qquad \omega_3 = 2113.6 \text{ cms}^{-1}$$

$$\omega_2 = 819.3 \text{ cms}^{-1} \qquad \omega_4 = 930.9 \text{ cms}^{-1}$$

The following are the normal equations used.

$$\lambda_1 - k_1 \left[\frac{1}{m_2} \right] = 0 \qquad \text{(non-degenerate vibration of type A)} \qquad (1)$$

$$\lambda_4 - \frac{k_H}{r^2} \left[\frac{1}{m_2} \right] = 0 \qquad \text{(doubly degenerate vibration of type E)} \qquad (2)$$

$$\lambda^2 - \lambda \left\{ k_1 \left[\frac{1}{m_2} + \frac{4}{3m_1} \right] + \left[\frac{3k_H \, k_\emptyset}{r^2(k_H + 3k_\emptyset)} \right] \left[\frac{1}{m_2} + \frac{4}{3m_1} \right] \right\}$$

$$+ \, k_1 \left[\frac{3k_H k_\emptyset}{r^2(k_H + 3k_\emptyset)} \right] \left[\frac{1}{m_2^2} + \frac{4}{m_1 m_2} \right] = 0 \qquad (3)$$

(triply degenerate vibrations of type E_2)

where $\lambda_i = 4\pi^2 c^2 \omega_i^2$ $\qquad$ ω_i = frequency in cms^{-1}

m_1 = mass of the germanium isotope

m_2 = mass of the hydrogen atom

k_1 = bond stretching constant of the Ge - H bond

r = the length of the Ge - H bond

k_H = the bond bending constant

$k_\emptyset$ = the orbital following constant.

The orbital following constant $k_\emptyset$ measures the 'power' of the orbitals to accommodate their orientation to the movements of the atoms in certain distortions.

The constants have been evaluated using the observed frequencies and the atomic weight of germanium 72.6 AMU. Since it was assumed that the observed frequencies were due to the most abundant isotope Ge^{74}, it was felt that the constants

should be re-evaluated on this basis. As can be seen in the

table, only one constant is isotope dependent. It changes by

	k_1	k_H/r^2	$k_\emptyset/r^2$
$Ge^{72.6}H_4$	2.61 x 10^5dynes/cm	5.15 x 10^5dynes/cm	5.07 x 10^4dynes/cm
$Ge^{74}H_4$	2.61 x 10^5dynes/cm	5.15 x 10^5dynes/cm	5.01 x 10^4dynes/cm

only about 1% when isotope 74 is substituted for the atomic weight

of germanium in the force equations. Such an error is usually

neglected since the observed frequencies may be incorrect by

as much as 10%.

Equations (1), (2), and (3) were next solved using the

corrected constants to find the vibrational frequencies of the

isotopic molecules $Ge^{70}H_4$ and $Ge^{76}H_4$. Again, it is noted that

only the triply degenerate vibrations depend on the mass of

the germanium atom. Equation (3) is a quadratic and hence its

roots are given by

$$\lambda = \frac{-B \pm\sqrt{B^2 - 4AC}}{2A}$$

where

$$-B = k_1\left[\frac{1}{m_2} + \frac{4}{3m_1}\right] + \left[\frac{3k_H k_\emptyset}{r^2(k_H + 3k_\emptyset)}\right]$$

$$\cdot\left[\frac{1}{m_2} + \frac{4}{3m_1}\right]$$

$$C = k_1 \left[\frac{3k_H k_{\varnothing}}{r^2(k_H + 3k_{\varnothing})} \right] \left[\frac{1}{m_2^2} + \frac{4}{m_1 m_2} \right]$$

$$A = 1$$

The values of the frequencies were found to be

	$\lambda_2 + \lambda_3 = -B$	$\lambda_2 \lambda_3 = C$	ω_2	ω_3
$Ge^{70}H_4$	$3.027 \times 10^5 \, secs^{-2}$	$1.0416 \times 10^{10} \, secs^{-4}$	$819.9 \, cms^{-1}$	$2113.5 \, cms^{-1}$
$Ge^{74}H_4$	$3.023 \times 10^5 \, secs^{-2}$	$1.0385 \times 10^{10} \, secs^{-4}$	$819.0 \, cms^{-1}$	$2113.0 \, cms^{-1}$
$Ge^{76}H_4$	$3.022 \times 10^5 \, secs^{-2}$	$1.0371 \times 10^{10} \, secs^{-4}$	$818.8 \, cms^{-1}$	$2112 \, cms^{-1}$

As usual it was necessary to correct the discrepancy between the calculated and observed values of $Ge^{74}H_4$ which are shown below.

	ω_2	ω_3
observed $Ge^{74}H_4$	$819.3 \, cms^{-1}$	$2113.6 \, cms^{-1}$
calculated $Ge^{74}H_4$	$819.0 \, cms^{-1}$	$2113.0 \, cms^{-1}$

After the frequencies have been corrected with appropriate factors they are, finally

	ω_1	ω_2	ω_3	ω_4
$Ge^{70}H_4$	$2090 \, cms^{-1}$	$820.2 \, cms^{-1}$	$2114.1 \, cms^{-1}$	$930.9 \, cms^{-1}$
$Ge^{76}H_4$	$2090 \, cms^{-1}$	$819.1 \, cms^{-1}$	$2112.6 \, cms^{-1}$	$930.9 \, cms^{-1}$

APPENDIX B

Calculations of $\frac{Q_2'}{Q_1'}$ for germanium-containing compounds,
which are summarized in this section, were made using the
Bigeleisen-Mayer equation developed in the theory and the
isotopic frequencies given in Appendix A. That is

$$\frac{Q_2'}{Q_1'} = \frac{\sigma_1}{\sigma_2}\left\{1 + \sum_i^{3n-6} G(u_i)\Delta u_i\right\}$$

where $G(u_i)$ has been previously defined. Values of this
function were taken from tables of Bigeleisen and Mayer (12).
The ratio of symmetry numbers is unity since only one atom in
each molecule is exchanged. Where a d-fold degeneracy in
frequency occurs it must be counted d times in the summation.
Finally, note that

$$\Delta u_i = \frac{hc}{kT}\Delta\omega_i$$

where $\Delta\omega_i$ is the frequency shift between the Ge^{70} and Ge^{76}
containing molecules.

TABLE V

Calculation of Q_2'/Q_1' for Germanium-Containing Diatomic Species

MOLECULE	TEMP $^\circ$C	u_{70}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$	Q_2'/Q_1'
$\underline{Ge^{76}S^{32}}$ $Ge^{70}S^{32}$	0	3.0407	3.0026	0.0381	0.21920	0.0084	1.0084
	25	2.7856	2.7507	0.0349	0.20469	0.0071	1.0071
	100	2.2255	2.1976	0.0279	0.16990	0.0047	1.0047
	250	1.5872	1.5673	0.0199	0.12557	0.0025	1.0025
$\underline{Ge^{76}Se^{80}}$ $Ge^{70}Se^{80}$	0	2.1685	2.1161	0.0524	0.16350	0.0086	1.0086
	25	1.9866	1.9386	0.0480	0.15225	0.0073	1.0073
	100	1.5871	1.5488	0.0383	0.12419	0.0048	1.0048
	250	1.1319	1.1046	0.0273	0.09023	0.0025	1.0025
$\underline{Ge^{76}Cl^{35}}$ $Ge^{70}Cl^{35}$	0	2.1524	2.1245	0.0279	0.16500	0.0046	1.0046
	25	1.9718	1.9463	0.0255	0.15279	0.0039	1.0039
	100	1.5753	1.5550	0.0203	0.12465	0.0025	1.0025
	250	1.1235	1.1090	0.0145	0.09057	0.0013	1.0013
$\underline{Ge^{76}Te^{130}}$ $Ge^{70}Te^{130}$	0	1.7238	1.6791	0.0447	0.13376	0.0060	1.0060
	25	1.5792	1.5383	0.0409	0.12341	0.0050	1.0050
	100	1.2617	1.2290	0.0327	0.09992	0.0033	1.0033
	250	0.8998	0.8765	0.0233	0.07312	0.0017	1.0017
$\underline{Ge^{76}F}$ $Ge^{70}F$	0	3.4960	3.4663	0.0297	0.24376	0.0072	1.0072
	25	3.2027	3.1755	0.0272	0.22868	0.0062	1.0062
	100	2.5587	2.5370	0.0217	0.19172	0.0042	1.0042
	250	1.8249	1.8094	0.0155	0.14314	0.0022	1.0022
$\underline{Ge^{76}Br}$ $Ge^{70}Br$	0	1.5758	1.5429	0.0329	0.12375	0.0041	1.0041
	25	1.4436	1.4134	0.0302	0.11403	0.0034	1.0034
	100	1.1534	1.1292	0.0242	0.09215	0.0022	1.0022
	250	0.8226	0.8054	0.0172	0.06640	0.0011	1.0011
$\underline{Ge^{76}O^{16}}$ $Ge^{70}O^{16}$	0	5.1755	5.1374	0.0381	0.31963	0.0122	1.0122
	25	4.7413	4.7064	0.0349	0.31120	0.0108	1.0108
	100	3.7879	3.7601	0.0278	0.25916	0.0072	1.0072
	250	2.7015	2.6816	0.0199	0.20257	0.0040	1.0040

For diatomic species $Q_2'/Q_1' = 1 + G(u)\Delta u$

TABLE VI

Calculation of Q_2'/Q_1' for $GeCl_4$ at $0°C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$ cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	397	397	0.00				
2	455.8	448.5	7.3	2.3631	0.03846	0.18073	0.0070
2	455.8	448.5	7.3	2.3631	0.03846	0.18073	0.0070
2	455.8	448.5	7.3	2.3631	0.03846	0.18073	0.0070
3	171.9	169.8	2.1	0.8947	0.01106	0.07358	0.0008
3	171.9	169.8	2.1	0.8947	0.01106	0.07358	0.0008
3	171.9	169.8	2.1	0.8947	0.01106	0.07358	0.0008
4	132	132	0.00				
4	132	132	0.00				

$$\sum_i G(u)\Delta u = 0.0233$$

$$Q_2'/Q_1' = 1.023 \text{ at } 0°C$$

TABLE VII

Calculation of Q_2'/Q_1' for $GeCl_4$ at $25°C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$ cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	397	397	0.00				
2	455.8	448.5	7.3	2.1684	0.03524	0.16771	0.0059
2	455.8	448.5	7.3	2.1684	0.03524	0.16771	0.0059
2	455.8	448.5	7.3	2.1684	0.03524	0.16771	0.0059
3	171.9	169.8	2.1	0.8196	0.01014	0.06755	0.0007
3	171.9	169.8	2.1	0.8196	0.01014	0.06755	0.0007
3	171.9	169.8	2.1	0.8196	0.01014	0.06755	0.0007
4	132	132	0.00				
4	132	132	0.00				

$$\sum_i G(u)\Delta u = 0.0197$$

$$Q_2'/Q_1' = 1.020 \text{ at } 25°C$$

TABLE VIII

Calculation of Q_2'/Q_1' for $GeCl_4$ at $100^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	397	397	0.00				
2	455.8	448.5	7.3	1.7295	0.02815	0.13741	0.0039
2	455.8	448.5	7.3	1.7295	0.02815	0.13741	0.0039
2	455.8	448.5	7.3	1.7295	0.02815	0.13741	0.0039
3	171.9	169.8	2.1	0.6548	0.00809	0.05418	0.0004
3	171.9	169.8	2.1	0.6548	0.00809	0.05418	0.0004
3	171.9	169.8	2.1	0.6548	0.00809	0.05418	0.0004
4	132	132	0.00				
4	132	132	0.00				

$$\sum_i G(u)\Delta u = 0.0129$$

$$Q_2'/Q_1' = 1.013 \text{ at } 100^{\circ}C$$

TABLE IX

Calculation of Q_2'/Q_1' for $GeCl_4$ at $250^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	397	397	0.00				
2	455.8	448.5	7.3	1.2335	0.02007	0.10027	0.0020
2	455.8	448.5	7.3	1.2335	0.02007	0.10027	0.0020
2	455.8	448.5	7.3	1.2335	0.02007	0.10027	0.0020
3	171.9	169.8	2.1	0.4670	0.00577	0.03878	0.0002
3	171.9	169.8	2.1	0.4670	0.00577	0.03878	0.0002
3	171.9	169.8	2.1	0.4670	0.00577	0.03878	0.0002
4	132	132	0.00				
4	132	132	0.00				

$$\sum_i G(u)\Delta u = 0.0066$$

$$Q_2'/Q_1' = 1.007 \text{ at } 250^{\circ}C$$

TABLE X

Calculation of Q_2'/Q_1' for $GeBr_4$ at $0^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$ cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	234	234	0.00				
2	333.5	325.1	8.4	1.7129	0.04426	0.13621	0.0060
2	333.5	325.1	8.4	1.7129	0.04426	0.13621	0.0060
2	333.5	325.1	8.4	1.7129	0.04426	0.13621	0.0060
3	111.7	110.6	1.1	0.5827	0.00580	0.04829	0.0003
3	111.7	110.6	1.1	0.5827	0.00580	0.04829	0.0003
3	111.7	110.6	1.1	0.5827	0.00580	0.04829	0.0003
4	78	78	0.00				
4	78	78	0.00				

$$\sum_i G(u)\Delta u = 0.0189$$

$$Q_2'/Q_1' = 1.019 \text{ at } 0^{\circ}C$$

TABLE XI

Calculation of Q_2'/Q_1' for $GeBr_4$ at $25^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$ cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	234	234	0.00				
2	333.5	325.1	8.4	1.5692	0.04054	0.12570	0.0051
2	333.5	325.1	8.4	1.5692	0.04054	0.12570	0.0051
2	333.5	325.1	8.4	1.5692	0.04054	0.12570	0.0051
3	111.7	110.6	1.1	0.5339	0.00531	0.04428	0.0002
3	111.7	110.6	1.1	0.5339	0.00531	0.04428	0.0002
3	111.7	110.6	1.1	0.5339	0.00531	0.04428	0.0002
4	78	78	0.00				
4	78	78	0.00				

$$\sum_i G(u)\Delta u = 0.0159$$

$$Q_2'/Q_1' = 1.016 \text{ at } 25^{\circ}C$$

TABLE XII

Calculation of $Q_2^!/Q_1^!$ for $GeBr_4$ at $100^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	234	234	0.00				
2	333.5	325.1	8.4	1.2537	0.03239	0.10183	0.0033
2	333.5	325.1	8.4	1.2537	0.03239	0.10183	0.0033
2	333.5	325.1	8.4	1.2537	0.03239	0.10183	0.0033
3	111.7	110.6	1.1	0.4265	0.00424	0.03544	0.0002
3	111.7	110.6	1.1	0.4265	0.00424	0.03544	0.0002
3	111.7	110.6	1.1	0.4265	0.00424	0.03544	0.0002
4	78	78	0.00				
4	78	78	0.00				

$$\sum_i G(u)\Delta u = 0.0103$$

$$Q_2^!/Q_1^! = 1.010 \text{ at } 100^{\circ}C$$

TABLE XIII

Calculation of $Q_2^!/Q_1^!$ for $GeBr_4$ at $250^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	234	234	0.00				
2	333.5	325.1	8.4	0.8941	0.02310	0.07355	0.0017
2	333.5	325.1	8.4	0.8941	0.02310	0.07355	0.0017
2	333.5	325.1	8.4	0.8941	0.02310	0.07355	0.0017
3	111.7	110.6	1.1	0.3042	0.00303	0.02531	0.0001
3	111.7	110.6	1.1	0.3042	0.00303	0.02531	0.0001
3	111.7	110.6	1.1	0.3042	0.00303	0.02531	0.0001
4	78	78	0.00				
4	78	78	0.00				

$$\sum_i G(u)\Delta u = 0.0053$$

$$Q_2^!/Q_1^! = 1.005 \text{ at } 250^{\circ}C$$

TABLE XIV

Calculation of Q_2'/Q_1' for GeF_4 at $0^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$ cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	738	738	0.00				
2	805.6	797.5	8.1	4.2019	0.04268	0.27720	0.0118
2	805.6	797.5	8.1	4.2019	0.04268	0.27720	0.0118
2	805.6	797.5	8.1	4.2019	0.04268	0.27720	0.0118
3	262.0	259.1	2.9	1.3652	0.01528	0.11037	0.0017
3	262.0	259.1	2.9	1.3652	0.01528	0.11037	0.0017
3	262.0	259.1	2.9	1.3652	0.01528	0.11037	0.0017
4	205	205	0.00				
4	205	205	0.00				

$$\sum_i G(u)\Delta u = 0.0406$$

$$Q_2'/Q_1' = 1.041 \text{ at } 0^{\circ}C$$

TABLE XV

Calculation of Q_2'/Q_1' for GeF_4 at $25^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$ cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	738	738	0.00				
2	805.6	797.5	8.1	3.8494	0.03910	0.26197	0.0102
2	805.6	797.5	8.1	3.8494	0.03910	0.26197	0.0102
2	805.6	797.5	8.1	3.8494	0.03910	0.26197	0.0102
3	262.0	259.1	2.9	1.2506	0.01400	0.10160	0.0014
3	262.0	259.1	2.9	1.2506	0.01400	0.10160	0.0014
3	262.0	259.1	2.9	1.2506	0.01400	0.10160	0.0014
4	205	205	0.00				
4	205	205	0.00				

$$\sum_i G(u)\Delta u = 0.0348$$

$$Q_2'/Q_1' = 1.035 \text{ at } 25^{\circ}C$$

TABLE XVI

Calculation of Q_2'/Q_1' for GeF_4 at $100^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	738	738	0.00				
2	805.6	797.5	8.1	3.0754	0.03124	0.22324	0.0070
2	805.6	797.5	8.1	3.0754	0.03124	0.22324	0.0070
2	805.6	797.5	8.1	3.0754	0.03124	0.22324	0.0070
3	262.0	259.1	2.9	0.9992	0.01183	0.08191	0.0010
3	262.0	259.1	2.9	0.9992	0.01183	0.08191	0.0010
3	262.0	259.1	2.9	0.9992	0.01183	0.08191	0.0010
4	205	205	0.00				
4	205	205	0.00				

$$\sum_i G(u)\Delta u = 0.0240$$

$$Q_2'/Q_1' = 1.024 \text{ at } 100^{\circ}C$$

TABLE XVII

Calculation of Q_2'/Q_1' for GeF_4 at $250^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	738	738	0.00				
2	805.6	797.5	8.1	2.19335	0.02228	0.16962	0.0038
2	805.6	797.5	8.1	2.19335	0.02228	0.16962	0.0038
2	805.6	797.5	8.1	2.19335	0.02228	0.16962	0.0038
3	262.0	259.1	2.9	0.71260	0.00798	0.05889	0.0005
3	262.0	259.1	2.9	0.71260	0.00798	0.05889	0.0005
3	262.0	259.1	2.9	0.71260	0.00798	0.05889	0.0005
4	205	205	0.00				
4	205	205	0.00				

$$\sum_i G(u)\Delta u = 0.0129$$

$$Q_2'/Q_1' = 1.013 \text{ at } 250^{\circ}C$$

TABLE XVIII

Calculation of Q_2'/Q_1' for GeH_4 at $0°C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$ cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	2090	2090	0.00				
2	820.2	819.1	1.1	4.3157	0.00579	0.28181	0.0016
2	820.2	819.1	1.1	4.3157	0.00579	0.28181	0.0016
2	820.2	819.1	1.1	4.3157	0.00579	0.28181	0.0016
3	2114.1	2112.6	1.5	11.1310	0.00790	0.41018	0.0032
3	2114.1	2112.6	1.5	11.1310	0.00790	0.41018	0.0032
3	2114.1	2112.6	1.5	11.1310	0.00790	0.41018	0.0032
4	930.9	930.9	0.00				
4	930.9	930.9	0.00				

$$\sum_i G(u)\Delta u = 0.015$$

$$Q_2'/Q_1' = 0.015 \text{ at } 0°C$$

TABLE XIX

Calculation of Q_2'/Q_1' for GeH_4 at $25°C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$ cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	2090	2090	0.00				
2	820.2	819.1	1.1	3.9537	0.00531	0.26663	0.0014
2	820.2	819.1	1.1	3.9537	0.00531	0.26663	0.0014
2	820.2	819.1	1.1	3.9537	0.00531	0.26663	0.0014
3	2114.1	2112.6	1.5	10.1972	0.00724	0.40197	0.0029
3	2114.1	2112.6	1.5	10.1972	0.00724	0.40197	0.0029
3	2114.1	2112.6	1.5	10.1972	0.00724	0.40197	0.0029
4	930.9	930.9	0.00				
4	930.9	930.9	0.00				

$$\sum_i G(u)\Delta u = 0.013$$

$$Q_2'/Q_1' = 1.013 \text{ at } 25°C$$

TABLE XX

Calculation of Q_2'/Q_1' for GeH_4 at $100^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	2090	2090	0.00				
2	820.2	819.1	1.1	3.1587	0.00424	0.22778	0.0010
2	820.2	819.1	1.1	3.1587	0.00424	0.22778	0.0010
2	820.2	819.1	1.1	3.1587	0.00424	0.22778	0.0010
3	2114.1	2112.6	1.5	8.1468	0.00578	0.37753	0.0022
3	2114.1	2112.6	1.5	8.1468	0.00578	0.37753	0.0022
3	2114.1	2112.6	1.5	8.1468	0.00578	0.37753	0.0022
4	930.9	930.9	0.00				
4	930.9	930.9	0.00				

$$\sum_i G(u)\Delta u = 0.009$$

$$Q_2'/Q_1' = 1.009 \text{ at } 100^{\circ}C$$

TABLE XXI

Calculation of Q_2'/Q_1' for GeH_4 at $250^{\circ}C$

i	ω_{70} cms^{-1}	ω_{76} cms^{-1}	$\Delta\omega$cms^{-1}	u_{76}	Δu	$G(u_{76})$	$G(u)\Delta u$
1	2090	2090	0.00				
2	820.2	819.1	1.1	2.2528	0.00303	0.17355	0.0005
2	820.2	819.1	1.1	2.2528	0.00303	0.17355	0.0005
2	820.2	819.1	1.1	2.2528	0.00303	0.17355	0.0005
3	2114.1	2112.6	1.5	5.8103	0.00413	0.33095	0.0014
3	2114.1	2112.6	1.5	5.8103	0.00413	0.33095	0.0014
3	2114.1	2112.6	1.5	5.8103	0.00413	0.33095	0.0014
4	930.9	930.9	0.00				
4	930.9	930.9	0.00				

$$\sum_i G(u)\Delta u = 0.006$$

$$Q_2'/Q_1' = 1.006 \text{ at } 250^{\circ}C$$

BIBLIOGRAPHY

1. Allenby, R. J., Geochim. et Cosmochim. Acta, $\underline{5}$, 40 (1954)

2. Aston, F. W., Nature, $\underline{111}$, 771 (1923)

3. Aston, F. W., Nature, $\underline{122}$, 167 (1928)

4. Aston, F. W., Proc. Roy. Soc. (London), $\underline{A\ 132}$, 487 (1931)

5. Aston, F. W., Phil. Mag. $\underline{38}$, 707 (1919); $\underline{39}$, 449 (1920); $\underline{42}$, 436 (1921)

6. Bach, F., Bonhoeffer, K. F., and Fajans, E., Zeit. für Physik. Chimie, $\underline{A\ 168}$, 313 (1934)

7. Bainbridge, K. T., J. Franklin Inst., $\underline{215}$, 509 (1933)

8. Bainbridge, K. T., Phys. Rev., $\underline{43}$, 1056 (1933)

9. Bardet, J. and Tchakarian, A., Compt. rend., $\underline{186}$, 637 (1928)

10. Bigeleisen, J., J. Chem. Phys., $\underline{17}$, 675 (1949)

11. Bigeleisen, J. and Friedmann, L., J. Chem. Phys., $\underline{17}$, 998 (1949)

12. Bigeleisen, J. and Mayer, M. G., J. Chem. Phys., $\underline{15}$, 261 (1947)

13. Bigeleisen, J. and Wolfsberg, M., "Advances in Chemical Physics," Vol. 1, Interscience Pub. Inc., New York.

14. Bleakney, W. and Gould, A. J., Phys. Rev., $\underline{44}$, 265 (1933)

15. Boltwood, Amer. J. Sci., $\underline{22}$, 537 (1906); $\underline{24}$, 370 (1907)

16. Carpenter, P. L., MacDonald, F., and Stuart, C. A. J. Bact., $\underline{30}$, 137 (1935)

17. Caunt, A. D., Short, L. N., and Woodward, L. A., Trans. Faraday Soc., 48, 873 (1952)

18. Claussen, W. H. and Hildebrand, J. H., J. Amer. Chem. Soc., 56, 1820 (1934)

19. Clayton, R. N., J. Chem. Phys. 30, 1246 (1959)

20. Craig, H. and Boato, G., Ann. Rev. Phys. Chem., 6, 403 (1955); Graig, H. Geochim. et Cosmochim. Acta 3, 53 (1953)

21. Dempster, A. J., Phys. Rev., 11, 316 (1918); 18, 415 (1921); 20, 631 (1922)

22. Dennis, L. M. and Hulse, R. E., J. Amer. Chem. Soc., 52, 3553 (1930)

23. Dennis, L. M. and Laubengayer, A. W., Z. physik. chem., 130, 520 (1927)

24. Eidinoff, M. L., Trans. N.Y. Acad. Sci., 16, 76 (1953)

25. Emeleús, H. J., James, F. W., King, A., Pearson, T. G., Purcell, R. H., and Briscoe, H. V. A., J. Chem. Soc., 1209 (1934)

26. Epstein, S., "Mass Spectrometry in Physics Research," National Bureau of Standards, Circular, 522, p. 133 (1953)

27. Epstein, S., Buchsbaum, R., Lowenstam, H. and Urey, H. C., Bull. Geol. Soc. Amer., 62, 417 (1953)

28. Evans, M. G. and Polanyi, M., Trans. Faraday Soc., 31, 875 (1935)

29. Everest, D. A., J. Chem. Soc., 4117 (1953)

30. Everest, D. A., Research Corresp., 8, A1 (1955)

31. Everest, D. A., private communication

32. Everest, D. A. and Terry, H., J. Chem. Soc., 2282 (1950)

33. Eyring, H., J. Chem. Phys., 3, 107 (1935)

34. Farkas, L. and Farkas, A., Naturwiss., 22, 218 (1934)

35. Franck,   and Urey, H. C., Science, <u>108</u>, 489 (1948)

36. Friedmann, I., Geochim. et Cosmochim. Acta., <u>4</u>, 89 (1953)

37. Geilmann, W. and Brünger, K., Biochem. Z., <u>275</u>, 387 (1935)

38. Graham, R. P., Macnamara, J., Crocker, I. H., and MacFarlane, R. B., Can. J. Chem., <u>29</u>, 89 (1951)

39. Grant, F. S., Geochimica et Cosmochimica Acta, <u>5</u>, 225 (1954)

40. Harrison, A. and Thode, H. G., Trans. Far. Soc., <u>54</u>, 84 (1948)

41. Heath, D. F. and Linnett, J. W., Trans. Far. Soc., <u>44</u>, 878 (1948)

42. Heath, D. F., Linnett, J. W., and Wheatley, P. J., Trans. Far. Soc., <u>46</u>, 137 (1950)

43. Herzberg, G., "Molecular Spectra and Molecular Structure," Vol. 1, D. Van Nostrand, Princeton, New Jersey

44. Herzberg, G., "Molecular Spectra and Molecular Structure," Vol. 2, D. Van Nostrand, Princeton, New Jersey

45. Hibbs, R. F., Redmond, J. W., Gwinn, H. R., and Harmon, W. D., Phys. Rev., <u>75</u>, 533 (1949)

46. Hirschfelder, J. O. and Wigner, J., J. Chem. Phys., <u>7</u>, 616 (1939)

47. Hoering, T. C., Science, <u>122</u>, 1233 (1955)

48. Inghram, M. G., Hayden, D. C., and Hess, R. J., Jr., Plutonium Project Report ANL-4082, 5 (1947 (from Graham <u>et al</u>)

49. Latimer, W. M., "Oxidation Potentials," Prentice-Hall, Inc., N.Y. (1950)

50. Lindsay, J. G., Bourns, A. N., and Thode, H. G., Can. J. Chem., <u>29</u>, 192 (1951); <u>30</u>, 163 (1952)

51. Lindsay, J. G., McElcheran, D. E., and Thode, H. G., J. Chem. Phys., <u>17</u>, 589 (1949)

52. Linnett, J. W. and Wheatley, P. J., Trans. Faraday Soc., 45, 39 (1949)

53. Macnamara, J., Fleming, W., Szabo, A., and Thode, H. G., Can. J. Chem., 30, 73 (1952)

54. Macnamara, J. and Thode, H. G., Phys. Rev., 78, 307 (1950)

55. Macnamara, J. and Thode, H. G., Research, 4, 582 (1951)

56. Marsden (1951) quoted in Rankama, "Isotope Geology," Pergamon Press (1954)

57. Mayer, J. E. and Mayer, M. G., "Statistical Mechanics," p. 207 ff., J. Wiley and Sons, Inc., N.Y.

58. McCrea, J. M., J. Chem. Phys., 18, 849 (1950)

59. Melander, L., "Isotope Effects on Reaction Rates," Ronald Press, N.Y. (1960)

60. Miller, L. P., Contrib. Boyce Thompson Inst., 15, 437 (1949)

61. Nier, A. O. and Gulbransen, E., J. Amer. Chem. Soc., 61, 697 (1939)

62. Piper, T. S. and Wilson, M. K., J. Inorg. Nucl. Chem., 4, 22 (1957)

63. Patnode, W. J. and Papish, J., J. Phys. Chem., 34, 1494 (1930)

64. Reynolds, J. H., Phys. Rev., 90, 1047 (1953)

65. Reynolds, J. H. and Verhoogan, J., Geochim. et Cosmochim. Acta, 3, 224 (1953)

66. Richards, T. W. and Lembert, M. C., J. Amer. Chem. Soc., 36, 1329 (1914)

67. Rittenburg, D., Bleakney, W., and Urey, H. C., J. Chem. Phys., 2, 48 (1934)

68. Ropp, G. A., Nucleonics, 10, #10, 22 (1952)

69. Shapiro, C. V., Gibbs, R. C., and Laubengayer, A. W., Phys. Rev., 40, 354 (1932)

70. Soddy, F., Chem. Soc. Ann. Rep., 7, 285 (1910)

71. Straley, J. W., Tindal, C. H., and Nielson, H. H., Phys. Rev., 62, 161 (1942)

72. Thode, H. G., Ann. Rev. Phys. Chem., 4, 95 (1953)

73. Thode, H. G., Kleerekoper, H., and McElcheran, D. E., Research, 4, 581 (1951)

74. Thode, H. G., Macnamara, J., and Collins, C. B., Can. J. Research, 27B, 361 (1949)

75. Thode, H. G., Wanless, H. K., and Wallouch, R., Geochim. et Cosmochim. Acta, 5, 286 (1954)

76. Thomson, J. J., "Rays of Positive Electricity and Their Applications to Chemical Analysis," Longmans, Green and Co. (1913)

77. Tilles, D., J. Geophys. Research, 66, 3015 (1961); 66, 3003 (1961)

78. Tudge, A. P. and Thode, H. G., Can. J. Research, 28B, 567 (1950)

79. Urey, H. C., J. Chem. Soc., 562 (1947)

80. Urey, H. C., Science, 108, 489 (1948)

81. Urey, H. C., Brickwedde, F. G., and Murphy, G. M., Phys. Rev., 39, 164 (1932); 39, 864 (1932)

82. Urey, H. C., Epstein, S., McKinney, C., and McCrea, J. M., Bull. Geol. Soc. Amer., 59, 1359 (1948)

83. Urey, H. C. and Grieff, L., J. Amer. Chem. Soc., 57, 321 (1935)

84. Urey, H. C. and Rittenburg, D., J. Chem. Phys., 1, 137 (1933)

85. Urey, H. C. and Teal, G. K., Rev. Mod. Phys., 7, 34 (1935)

86. Urey, H. C. and Washburn, E. W., Proc. Nat. Acad. Sci.,
        $\underline{18}$, 496 (1932)

87. Wanless, R. K. and Thode, H. G., Journal Sci. Inst.,
        $\underline{30}$, 395 (1953)

88. Weber, L. A., Wahl, M. H., and Urey, H. C., J. Chem.
        Phys., $\underline{3}$, 129 (1935)

89. Wolfsberg, M., J. Chem. Phys., $\underline{33}$, 21 (1960)